mL of absolute ethanol was slowly warmed to reflux under an atmosphere of nitrogen. After 1 h the violet solution became organge; the mixture was cooled, and the solvent was removed in vacuo. The remaining orange oil was dissolved in 50 mL of CH_2Cl_2, washed with 50 mL of 2 N NaOH and water, and dried with sodium sulfate. The solvent was removed, and the residue was purified by chromatography on Al_2O_3 BIII (Brockmann) with CH_2Cl_2. The first orange fraction was collected. After removal of the solvent in vacuo, the orange residue was twice recrystallized from ethanol to give 234 mg (61%) of 1-diazocyclopent[*cd*]azulene-2-one (**4**) as dark brown needles: mp 115 °C; IR (KBr) 2061, 1715, 1695, 1668, 1652, 1596, 1568, 1538, 1520, 1506, 1455, 1446, 1425, 1375, 1313, 1261, 1229, 1153, 1031, 847, 790, 750, 731, 635, 588, and 422 cm^{-1}; UV (Ar-Matrix) λ_{max} 435, 422, 408, 397, 385, 354, 337, 320, 302, 279, 267, 239, and 230 nm; ^1H NMR ($CDCl_3$) δ 8.4–7.3 (m); high-resolution mass spectrum; calcd for $C_{12}H_6N_2O$ 194.0481, found 194.0476. The sample was sublimed at 80 °C (10^{-6} torr) and codeposited with argon to form a matrix.

1,2,3-*H*-2-Diazophenalene-1,3-dione (15). The diazodione was prepared by the method of Regitz[64] and gave analytical data as reported. The sample was sublimed at 91 °C (10^{-6} torr) and codeposited with argon to form a matrix.

1,2-Dihydroacenaphthylene-5,6-dicarboxylic Anhydride (16). The anhydride was prepared by the method of Carpino and Gowecke[29] as modified by Trost.[30] The infrared spectrum of **16** could not be obtained under argon-matrix isolation conditions due to the low volatility of the sample.

Acenaphthlene-5,6-dicarboxylic Anhydride (18). A stirred suspension of dimethyl acenaphthylene-5,6-dicarboxylate[29] (5.0 g, 18.7 mmol) in 100 mL of 60% aqueous sulfuric acid was warmed to reflux. After 45 min, the red-orange suspension was cooled to room temperature and vacuum-filtered through a glass-fritted funnel to give anhydride **18** as an orange-red solid (4.05 g, 98%): mp >230 °C; IR (KBr) 2913, 2849, 1774, 1765, 1735, 1710, 1690, 1649, 1624, 1569, 1559, 1548, 1539, 1519, 1501, 1489, 1458, 1443, 1409, 1369, 1348, 1298, 1262, 1227, 1213, 1200, 1152, 1128, 1099, 1050, 987, 959, 857, 807, 749, 734, 694, 669, 644, 498, 411, 361, 350, and 319 cm^{-1}; UV (95% EtOH) λ_{max} 360 and 240 nm; high-resolution mass spectrum, calcd for $C_{14}H_6O_3$ 222.0317, found 222.0326. The infrared spectrum of **18** could not be obtained under argon-matrix isolation conditons due to the low volatility of the sample.

(64) Regitz, M. *Liebigs Ann. Chem.* **1964**, *676*, 101–109.

Acknowledgment. This research was supported by Grant CHE81-11196 from the National Science Foundation and by a grant from the International Business Machine Corporation. We are grateful to Dr. Curtis Kreil for technical assistance with the matrix isolation ESR apparatus and Professor Klaus Hafner for a sample of cyclopent[*cd*]azulene-2-one (**21**). Predoctoral fellowships (R.J.M.) were provided by the National Science Foundation (1980–1983) and the International Business Machine Corporation (1983–1984). H.P.K. is a Feodor Lynen Postdoctoral Fellow of the Alexander von Humboldt Foundation.

Registry No. 1, 2008-77-7; **2**, 87985-99-7; **3**, 87986-00-3; **4**, 98361-78-5; **5**, 98361-79-6; **6**, 98361-80-9; **8**, 98361-81-0; **9**, 82515-17-1; **10**, 86998-10-9; **11**, 87016-12-4; **12**, 98361-82-1; **13**, 81-84-5; **14**, 98361-83-2; **15**, 18931-19-6; **16**, 5699-00-3; **17**, 98361-84-3; **18**, 21973-76-2; **19**, 98361-85-4; **20**, 98361-86-5; **21**, 52711-37-2; acenaphthylene-1,2-dione, 82-86-0; *p*-toluenesulfonyl hydrazide, 1576-35-8; acenaphthylene-1,2-dione mono-*p*-toluenesulfonylhydrazone, 66365-89-7; 5,6-dihydrocyclopent[*fg*]acenaphthylene-1,2-dione, 5254-01-3; 5,6-dihydrocyclopent[*fg*]acenaphthylene-1,2-dione mono-*p*-toluenesulfonylhydrazone, 98361-87-6; cyclopent[*fg*]acenaphthylene-1,2-dione, 5253-87-2; cyclopent[*fg*]-acenaphthylene-1,2-dione mono-*p*-toluenesulfonylhydrazone, 98361-87-6; cyclopent[*cd*]azulen-1,2-dione, 52711-38-3; dimethyl acenaphthylene-5,6-dicarboxylate, 92964-95-9.

Mechanism of the Chromium-Catalyzed Epoxidation of Olefins. Role of Oxochromium(V) Cations

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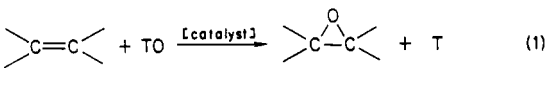
Contribution from the Chemistry Department, University of Houston, University Park, Houston, Texas 77004. *Received April 29, 1985*

Abstract: The catalytic epoxidation of various olefins with iodosylbenzene is efficiently carried out by a series of chromium(III) cations Cr^{III}(salen)$^+$ (I) which are promoted by pyridine *N*-oxide (pyO) and related oxygen donors as the cocatalyst. Analysis of the catalytic rate profile and products establish the oxochromium(V) derivative O=Cr(salen)$^+$ (II) and its donor adduct O=Cr(salen)(pyO)$^+$ (III) as the reactive intermediates in the catalytic cycle. The successful isolation as well as the complete spectral analysis and structural characterization by X-ray crystallography of both II and III reveal the basis for oxygen activation in the O=Cr^V functionality. The mechanism of oxygen atom transfer involves the rate-limiting attack on the olefin by the electrophilic oxochromium(V) cation. The observation of benzaldehyde as a byproduct derived from the pyO-promoted C=C cleavage of styrene provides a method for unequivocally proving the existence of a transient intermediate during oxygen atom transfer. Thus the rate of olefin oxidation is found to be completely independent of the product-forming steps leading to epoxide and benzaldehyde, as they are modulated by added pyO. Steric effects, isotopic ^{18}O tracers, stereochemistry, skeletal rearrangement, and substituent effects all provide mechanistic probes for the structure of the metastable intermediate.

The catalytic functionalization of various types of hydrocarbons with such terminal oxidants (TO) as dioxygen, peroxides, nonmetal oxides, etc., is of both chemical and biochemical importance.[1] Among such transformations, the metal-catalyzed conversion of an olefin to its epoxide by oxygen atom transfer poses an intriguing synthetic as well as theoretical challenge.[2] In this regard Groves and co-workers have introduced the interesting notion of oxygen rebound, in which the oxygen atom is successively transferred from the terminal oxidant to the metal catalyst and thence to the olefin.[3] Accordingly, a crucial role is played by a reactive oxometal intermediate for which there is recent experimental support.[4]



(1)

(1) For a review, see: Sheldon, R. A.; Kochi, J. K. "Metal-Catalyzed Oxidations of Organic Compounds"; Academic: New York 1981.

(2) See: Berti, G. "Topics in Stereochemistry"; Allinger, N. L., Eliel, E. L. Eds.; Wiley: New York, 1973; Vol. V. Rappe', A. K.; Goddard, W. A., III *J. Am. Chem. Soc.* **1982**, *104*, 3287.

(3) (a) Groves, J. T.; McClusky, G. A. *J. Am. Chem. Soc.* **1976**, *98*, 859. (b) Groves, J. T.; Nemo, T. E.; Myers, R. S. *J. Am. Chem. Soc.* **1979**, *101*, 1032. (c) See also: Guengerich, F. P.; McDonald, T. L. *Acc. Chem. Res.* **1984**, *17*, 9.

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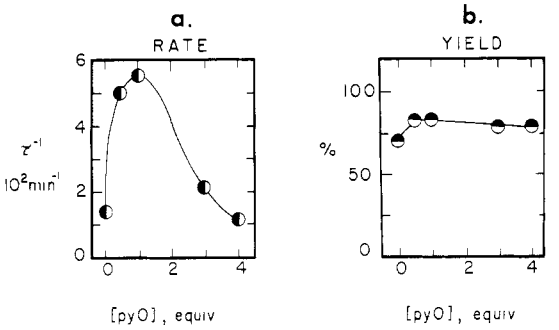


Figure 1. Effect of pyridine *N*-oxide on (a) the rates of epoxidation and (b) the yields of norbornene oxide derived from the oxochromium(V) complex IIb (0.011 mmol), norbornene (0.10 mmol), and iodosylbenzene (0.055 mmol) in acetonitrile at 25 °C.

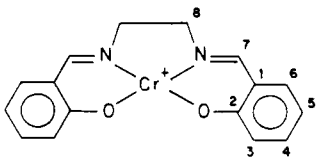
In this study we wish to followup on a preliminary report of the actual isolation and structure determination of a series of catalytically active oxometal species.[5] Thus we found that oxochromium(V) complexes can be generated from various well-characterized chromium(III) complexes ($Cr^{III}L$) with iodosylbenzene.[6] Our principal focus now is to demonstrate how the

$$Cr^{III}L + PhIO \rightarrow O{=}Cr^{V}L + PhI \qquad (2)$$

oxometal species enters the catalytic cycle and to delineate the mechanism of oxygen atom transfer from the oxometal to the olefin substrate.

Results

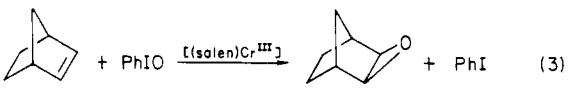
The chromium catalysts used in this study derive from a series of cationic salen complexes (Ia–h) of the general structure[7]



Ia, 8,8,8',8', $-H_4$
b, 8,8,8',8', $-(CH_3)_4$
c, 5,5', $-(Cl)_2$
d, 7,7' $-(CH_3)_2$
e, 7,7', $-(Ph)_2$
f, 5,5', $-(Cl)_2-8,8,8',8'-(CH_3)_4$
g, 5,5', $-(CH_3O)_2-8,8,8',8'-(CH_3)_4$
h, 4,4', 6,6' $-(CH_3O)_4-8,8,8',8'-(CH_3)_4$

with substituents on the aromatic rings (4, 5, or 6-positions), the methine carbon (7) and/or the ethano bridge (8). We utilized iodosylbenzene as the terminal oxidant owing to its sparing solubility in acetonitrile.[8] Furthermore, it allowed the course of epoxidation to be readily monitored by gas chromatographic analysis of its innocuous reduction product iodobenzene. The applicability of the chromium(III)-catalyzed epoxidation of olefins with iodosylbenzene is presented first, and it is followed by detailed mechanistic studies of the formation, isolation, and properties of the oxochromium(V) intermediate as the active agent in the epoxidation step.

I. Catalytic Epoxidation of Olefins with (salen)Cr^{III}. Optimum conditions for the catalytic epoxidation were initially developed with norbornene. Thus an orange solution of 0.01 M (salen)Cr^{III} in acetonitrile containing excess norbornene immediately turned dark green-black upon the addition of 5 equiv of iodosylbenzene. Continued stirring of the heterogeneous reaction mixture at 25 °C eventually led back to the homogeneous orange solution, from which norbornene oxide could be isolated in ~70% yields according to the stoichiometry in eq 3.[9] This sequence of rather



(3)

dramatic color changes could be expedited by the judicious addition of pyridine *N*-oxide. Indeed the presence of 0.5–1 equiv of pyridine *N*-oxide accelerated the rate of epoxidation, but further amounts led to its retardation, as shown in Figure 1a. By contrast, the yield of norbornene oxide is not strongly influenced by the presence of pyridine oxide (see Figure 1b).

Any mechanistic formulation of the catalytic epoxidation must account for the dichotomous effect of additives such as pyridine oxide.[10] Before doing so, however, we list in Table I the yields of epoxides obtained from the chromium-catalyzed reaction of various olefins with iodosylbenzene in acetonitrile solution under a standard set of conditions. The catalytic epoxidation can also be carried out with (salen)Cr^{III} in methylene chloride solutions with the aid of pyridine as the cocatalyst.[11] The yields of various epoxides follow the same trend shown in Table I.

II. Oxidative Conversion of Chromium(III) to Oxochromium(V) Species. The chromium(III) complexes I are readily converted to the corresponding oxochromium(V) species II by iodosylbenzene under the reaction conditions of the catalytic process described in eq 3. For example, the exposure of the various (salen)Cr^{III} complexes listed in Table II to a suspension of iodosylbenzene in acetonitrile consistently led to an immediate darkening of the orange solutions to dark green-black. The latter corresponds to the presence of a long tail extending beyond 800 nm in the visible absorption spectra shown in Figure 2. In particular, the absorption

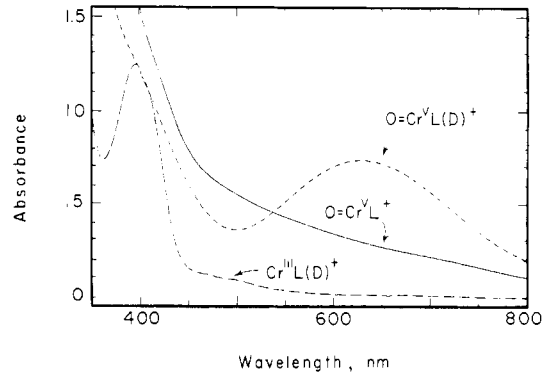


Figure 2. Electronic absorption spectra of (a) the oxochromium(V) complex IIb (3×10^{-3} M), (b) its pyridine *N*-oxide adduct, and (c) the resultant (Me_4salen)Cr^{III} product derived after the reaction with norbornene in acetonitrile.

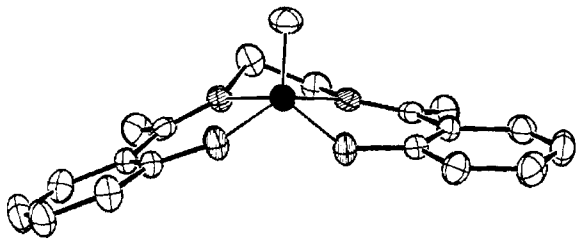


Figure 3. ORTEP diagram of the oxochromium(V) cation IId. [The hydrogen atoms are omitted for clarity.]

(4) (a) Groves, J. T.; Kruper, W. J., Jr. *J. Am. Chem. Soc.* **1979**, *101*, 7613. (b) Groves, J. T.; Myers, R. S. *J. Am. Chem. Soc.* **1983**, *105*, 5791. (c) Smegal, J. A.; Hill, C. L. *J. Am. Chem. Soc.* **1983**, *105*, 3515. (d) Yuan, L. C.; Bruice, T. C. *J. Am. Chem. Soc.* **1985**, *107*, 512, for leading references.

(5) Siddall, T. L.; Miyaura, N.; Kochi, J. K. *J. Chem. Soc., Chem. Commun.* **1983**, 1185.

(6) The salen ligand (bis-salicyladehyde ethylenimine) is hereafter designated generically as L.

(7) (Trifluoromethane)sulfonate (triflate) or hexafluorophosphate is the counter anion.

(8) Although the solubility of iodosylbenzene in CH_3CN is low ($<10^{-4}$ mM), the rate of oxygen atom transfer of I is sufficiently fast to allow solubilization within 5–10 min under appropriate conditions (vide infra).

(9) Chromium(III) also catalyzes the decomposition of iodosylbenzene, presumably by attack on solvent.

(10) In general we found oxygen donor ligands such as pyridine *N*-oxide and its derivatives, phosphine oxides, sulfoxides, hexamethylphosphortriamide, *N*,*N*-dimethylformamide, etc., to lead to the catalytic enhancement of epoxidation.

(11) See the results listed in Table I of ref 5.

Table I. The Chromium-Catalyzed Epoxidation of Olefins[a]

olefin	epoxide	yield,[b] %
norbornene		85
styrene		40
β-methylstyrene		
Z		46[c]
E		52[d]
stilbene		
Z		44[e]
E		58[f]
cyclooctene		49
cyclohexene		2[g]
hexene-2		
Z		10[h]
E		4[i]
octene		<1[a]

[a] In acetonitrile solution with 0.011 mmol salenCr$^+$OTf$^-$, 1.1 mmol olefin, 0.055 mmol PhIO and 0.006 mmol *N*-pyridine oxide at 25 °C. [b] Based on PhI produced. [c] In addition to 2% *E* isomer, 14% $PhCH_2CHO$ and 7% PhCHO. [d] In addition to 11% PhCHO and <0.5% *Z* isomer. [e] In addition to 3% *E* isomer and 5% PhCHO. [f] In addition to 1% PhCHO and <0.5% *Z* isomer. [g] In addition to 1% cyclohexenol and 2% cyclohexenone. [h] In addition to 4% *E* isomer and other isomer products. [i] Contains <0.2% *Z* isomer. [j] In addition to unidentified products in low yields.

Table II. Spectral Parameters and Magnetic Susceptibility of Oxochromium(V) Complexes II[a]

oxochromium(V) complex	$\nu_{C=O}$,[b] cm^{-1}	Hfs,[c] G		μ_{eff},[d] μ_B
		a_N	a_{Cr}	
IIa	998	2.17	19.42	1.75
IIb	1007	2.12	20.00	1.76
IIc	1007	2.15	19.50	1.82
IId	1003	2.15	19.35	1.85
IIe	985	2.05	19.25	1.86

[a] As the (trifluoromethane)sulfonate salt. [b] Nujol mull. [c] Isotropic hyperfine splittings in acetonitrile solution. $\langle g \rangle$ values = 1.978 (IIa), 1.977 (IIb), 1.978 (IId), 1.978 (IId), 1.978 (IIe). [d] Evans method (ref 15) in acetonitrile.

band of the oxochromium(V) IIa consists of a partially resolved maximum at ~550 nm. The absorption maximum of the tetramethyl analogue IIb in Figure 2 appears to be blue shifted under the ligand absorptions.

The oxochromium(V) complex IId was isolated as a single crystal suitable for X-ray crystallography from the treatment of the (salen)Cr^{III} complex Id with iodosylbenzene, i.e.

$$\underset{\text{Id}}{Cr^{III}(Me_2salen)^+OTf^-} + PhIO \rightarrow \underset{\text{IId}}{O{=}Cr^{V}(Me_2salen)^+OTf^-} + PhI \quad (4)$$

followed by precipitation with diethyl ether and recrystallization

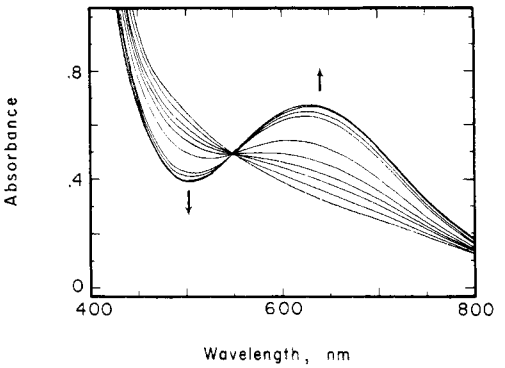


Figure 4. The formation of the pyridine *N*-oxide adduct IIIb of the oxochromium(V) cation IIb (1.2×10^{-3} M) in acetonitrile solutions. Spectra (from bottom to top) correspond to the addition of 0, 1, 2, 3, 5, 10, 30, 40, 60, 70, and 80 equiv of pyO.

from a mixture of acetonitrile and chlorobenzene.[12] The ORTEP diagram in Figure 3 clearly shows the presence of the oxo functionality on the chromium center displaced ~0.5 Å above the mean salen plane to describe a roughly square-pyramidal coordination.[13] The oxochromium functionality is characterized by an infrared absorption (stretch) at 1003 cm^{-1}, which is displaced to 963 cm^{-1} upon isotopic substitution with oxygen-18.[14] Furthermore, the presence of the d^1 electron configuration characteristic of a chromium(V) complex is indicated both by the magnetic susceptibility of 1.85 μ_B,[15] and an isotropic ESR spectrum showing well-resolved nitrogen (a_N = 2.15 G) and chromium (a_{Cr} = 19.35 G, $I = {}^3/_2$ for ^{53}Cr in 9.55% natural abundance) splittings centered at $\langle g \rangle$ = 1.978 at 25 °C. The variation in these spectral parameters with ring and side-chain substitution on the salen ligand is included in Table II for some typical derivatives.[13]

The oxochromium(V) complexes show widely varying stabilities in acetonitrile solution. On one hand, tetramethyl substitution on the ethano bridge increases the stability of **IIa** in acetonitrile from 10 to >30 days. However, dimethyl substitution on the methine (7) position decreases the stability of IIa by 5-fold. Among the 5,5′-substituted analogues of tetramethylsalen IIb, the stability decreases precipitously in the order Cl ~ H ≫ CH_3O > NO_2, such that the oxo derivative of 5,5′-dinitro-(8,8,8′,8′-tetramethylsalen)chromium(III) is a highly transient species with a lifetime of <10 min, as detected by its characteristic ESR spectrum. Decomposition appears to affect the salen moiety permanently since the oxochromium(V) functionality is not regenerated with additional iodosylbenzene.[17]

III. Coordination of Oxochromium(V) with Donor Ligands. Oxochromium(V) species are prone to the coordination of various types of donor ligands (D). Thus the addition of pyridine *N*-oxide to a solution of oxochromium(V) IIb causes an immediate change in color to emerald green, which arises from a red shift in the absorption spectrum shown in Figure 4. For example, the addition of successive incremental amounts of pyridine oxide leads to a

(12) Most of the (salen)Cr^{III} complexes afforded crystals of the oxochromium(V) derivatives which were unsuitable for X-ray crystallography, being either microcrystalline, twinned, or disordered (see ref 5).

(13) Srinivasan, K.; Kochi, J. K. *Inorg. Chem.*, in press.

(14) Compare with $\nu_{O=Cr}$ 1026 and 982 cm^{-1} for the ^{16}O and ^{18}O isotopes, respectively, in the porphyrin complexes.[4a]

(15) (a) The calculated spin-only value of μ_{eff} for a d^1 species is 1.73 μ_B. (b) Determined by the Evans method. Evans, D. F. *J. Chem. Soc.* **1959**, 2003. See also: Jolly, W. L. "The Synthesis and Characterization of Inorganic Compounds"; Prentice-Hall: Englewood Cliffs, NJ, 1971; pp 375–378.

(16) Isotropic $\langle g \rangle$ values in the range 1.978–1.988 have been reported for a variety of chromium(V) species. See: Kon, J. H. *J. Inorg. Nucl. Chem.* **1963**, *25*, 933. Krumpolc, M.; DeBoer, B. G.; Rocek, J. *J. Am. Chem. Soc.* **1978**, *100*, 145. Freeman, F.; Armstead, C. R.; Essig, M. G.; Karchefski, E. M.; Kojima, C.; Manopolie, V. C.; Wickman, A. H. *J. Chem. Soc., Chem. Commun.* **1980**, 65. Wiberg, K. B.; Schaefer, H. *J. Am. Chem. Soc.* **1969**, *91*, 933. Garifyanov, N. S.; Kozyrev, B. M.; Fedofov, V. N. *Dokl. Akad. Nauk. SSSR* **1968**, *178*, 808.

(17) The products of the decomposition of oxochromium(V) species in either acetonitrile or methylene chloride have not been investigated.[9] The possibility of oxochromium(IV) has been considered.[13]

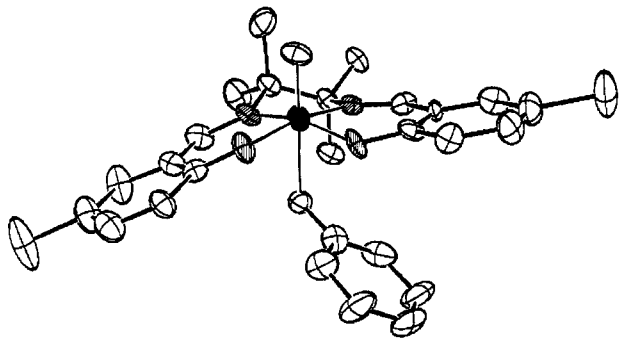


Figure 5. ORTEP diagram of the oxochromium(V) adduct IIIf with pyridine *N*-oxide as the donor ligand.

well-defined absorption band at λ_{max} 625 nm (ϵ 2450 M^{-1} cm^{-1}) and an isosbestic point at 550 nm. The new species also shows a well-resolved ESR spectrum which is shifted to slightly higher fields at $\langle g \rangle = 1.975$ from its precursor, but with only slightly altered hyperfine splittings (a_N = 1.94 G, a_{Cr} = 19.79 G). Quantitative analysis of either the visible absorption or the ESR spectral data afforded the formation constant $K = 75$ M^{-1} for the 1:1 adduct IIIb,[18] where D and L are pyridine *N*-oxide and Me_4salen, respectively.[6]

$$\underset{\text{II}}{O{=}Cr^{V}L^{+}} + D \overset{K}{\rightleftharpoons} \underset{\text{III}}{O{=}Cr^{V}L(D)^{+}} \qquad (5)$$

The addition of triphenylphosphine oxide to the oxochromium(V) species IIb caused a similar change in the visible absorption spectrum. However, the formation constant of 13 M^{-1} for this 1:1 adduct is smaller than that of the pyridine oxide analogue. The trend in the formation constants indicates a substantial steric inhibition of adduct formation.[13] It is also noteworthy that water affords the weakest complex, even by comparison among other oxygen-donor ligands such as dimethyl sulfoxide, hexamethylphosphortriamide and dimethylformamide.

A single crystal of the donor adduct III of oxochromium(V) with pyridine *N*-oxide was successfully grown under a carefully controlled set of conditions (see Experimental Section).[19] The ORTEP diagram of the oxochromium(V) adduct IIIf in Figure 5 shows the completion of the octahedral coordination of the chromium center by the pyridine *N*-oxide ligand.[13] It is noteworthy that the principal structural difference between oxochromium(V) and its donor adduct is found in the coordination sphere of chromium, since the salen ligands in Figures 3 and 6 are the same despite the changing substitution patterns on the periphery. The Cr atom, which is displaced 0.53 Å above the salen plane in the 5-coordinate complex,[20] is pulled back to 0.26 Å by axial ligation; and there is a concomitant increase in the bond lengths to the pair of equatorial salen oxygens which results in an increase in the ligand "bite". The long bond to pyridine oxide (Cr–Opy 2.18 Å) probably reflects the high trans influence of the oxo ligand. Although the Cr–oxo bond length increases by only 0.01 Å upon ligation, the weakening of this bond is readily apparent in the infrared spectrum by a shift of $\nu_{Cr=O}$ from 1004 cm^{-1} in IIf to 943 cm^{-1} in the pyridine oxide adduct or by ~0.2 kcal mol^{-1} to lower energy.[22]

IV. Stoichiometric Epoxidation of Olefins with Oxochromium(V). Effect of Donor Ligands. Oxochromium(V) is

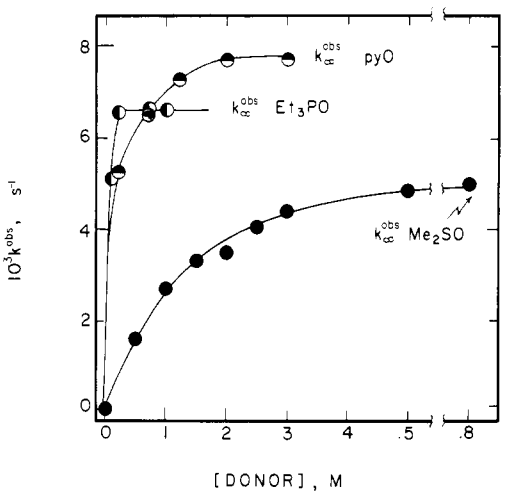
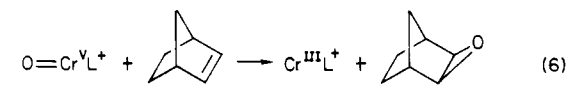


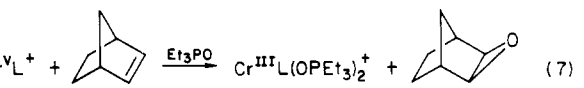
Figure 6. Limiting rates of epoxidation of norbornene (0.10 M) with the oxochromium(V) cation IIb (0.003 M) in the presence of incrementally increasing amounts of donor ligands: (a) pyridine *N*-oxide, (b) triethylphosphine oxide, and (c) dimethyl sulfoxide in acetonitrile.

capable of the direct epoxidation of olefins, the course of which is easily followed by the marked color change of the acetonitrile solution from dark green-black to orange (see Figure 2). In order to develop some optimum reaction conditions for effecting this oxygen atom transfer, we initially examined norbornene and styrene in detail and found two factors to be especially important—namely the concentration of oxochromium(V) and the presence of donor ligands D. For example, norbornene was epoxidized in high yield (>90%) when dilute solutions of <0.02 M oxochromium(V) complex IIb were employed.[23] The isolation of the original chromium(III) complex Ib in 98% yield[24] indicated the stoichiometry for epoxidation to be



(6)

However, the same epoxidation carried out with an increased (6-fold) concentration of IIb afforded only 60% norbornene oxide. Next, the addition of donor ligands led to a dramatic enhancement in the rate of epoxidation as well as to an increased yield of epoxide. Thus the presence of pyridine oxide (0.02 M) during the epoxidation described in eq 6 led to a decrease in the time required for completion from >15 h to less than 45 min and a concomitant increase in the epoxide yield from 90% to 100%. A similar cocatalytic effect was noted with triethylphosphine oxide. In the latter case, the Cr-containing product was identified as the inner-sphere complex,[25] and it was isolated in 90% yield, i.e.



(7)

where $Cr^{III}L$ is derived from Ib.[26]

The reactivity of various olefins toward the oxochromium(V) species IIb was examined under standard conditions. Some typical results with pyridine *N*-oxide as the cocatalyst are presented in Table III.

(18) The results do not accord with 2:1 or higher adducts. See also Figure 5.

(19) Among the various oxochromium(V) cations and donor ligand we had available, we were successful in growing a single crystal only from IIf and pyridine *N*-oxide.

(20) The length of the Cr=O bond has been reported to lie in the range 1.52–1.55 Å.[21]

(21) For a review, see: Mitewa, M.; Bontchev, P. R. *Coord. Chem. Rev.* **1985**, *61*, 281. See also: Griffith, W. P. *Coord. Chem. Rev.* **1970**, *5*, 459.

(22) For example, the band in IIf shifts from 1004 to 943 cm^{-1} upon complexation with pyridine oxide in CH_3CN. Confirmation of these band assignments to Cr=O was obtained from the ^{18}O-labeled derivatives, in which these bands were shifted to 965 and 901 cm^{-1}, respectively.

(23) With a 10-fold excess or norbornene.

(24) Isolated as the bis-aquo complex (salen)$Cr(OH_2)_2^+$ after the addition of water.

(25) The isolation of $Cr^{III}L(OPEt_3)_2$ indicates that the cocatalyst entered the coordination sphere of oxochromium(V) prior to oxygen from transfer since its rate of incorporation into the substitution-inert $Cr^{III}L$ is too slow.

(26) Related donors such as triphenyl- and tributylphosphine oxides, dimethyl sulfoxide, and hexamethylphosphortriamide are similarly effective, while anionic ligands such as fluoride, chloride, cyanate, and trifluoroacetate increased the reaction rate but afforded lower yields of epoxide. Pyridine was less effective than pyridine *N*-oxide, and trimethylamine oxide caused a rapid decomposition of IIb and afforded only traces of epoxide. Use of methylene chloride, dimethyl sulfoxide, acetone, or *N*,*N*-dimethylformamide as solvent generally led to inferior yields of epoxide.

Table III. Stoichiometric Epoxidation of Olefins with Oxochromium(V)[a]

olefin	epoxide	yield[b]
norbornene		100
styrene[c]		78[d]
β-methylstyrene[c,g]		
Z		55[e]
E		86[f]
stilbene[q]		
Z		47[h]
E		81[i]
cyclooctene[c]		70
cyclohexene[j]		22[k]
hexene-2[m]		
Z		45[n]
E		20[p,q]
octene-1[j]		12[q]

[a] In acetonitrile containing 0.02 M IIb, 0.20 M pyridine *N*-oxide, and 0.2 M olefin, unless stated otherwise. [b] Based on IIb charged. [c] 0.08 M pyridine oxide. [d] In addition to 11% phenylacetaldehyde and 6% benzaldehyde. [e] In addition to 3% *E* isomer, 11% benzyl methyl ketone, and 4% benzaldehyde. [f] No *Z* isomer (<0.2%) but 7% benzaldehyde. [g] Recovered olefin was unrearranged. [h] In addition to 2% *E* isomer and 10% benzaldehyde. [i] No *Z* isomer, but 10% benzaldehyde formed. [j] 2.0 M olefin. [k] In addition to 3% cyclohexenol and 19% cyclohexenone. [m] 1.0 M olefin. [n] In addition to 10% *E* isomer. [p] No *Z* isomer (<0.2%). [q] Other unidentified products in low yields.

Substituents on the salen ligand play an important role in determining the effectiveness of oxochromium(V) species. For example, those oxochromium(V) complexes which contain the permethylated ethano bridge (e.g., IIb,f,g,h) are among the most effective epoxidizing agents, since they effect high conversions of both norbornene and styrene.[27] By contrast, the parent complex IIa and its relatives IIc,d,e effect styrene conversions of only 17%, 50%, 8%, and 41%, respectively, under the same conditions.[27b]

Substituents on the salen ligand also affect the oxidation of styrene by altering the formation of two side products—viz., phenylacetaldehyde and benzaldehyde. Phenylacetaldehyde represents the oxidative rearrangement of styrene, and benzaldehyde derives from the scission of its olefinic linkage. First, phenylacetaldehyde is a product of direct oxidation, and it also results from the subsequent isomerization of styrene oxide under reaction conditions.[28] The latter pathway is markedly suppressed by the presence of pyridine oxide and related additives, as shown by the results in Table IV. Control experiments establish that the residual phenylacetaldehyde does not arise from styrene oxide.[29] Second, the amount of benzaldehyde formed is highly

(27) (a) For example, norbornene oxide is formed in 95, 95, and 75% from IIb, IId, and IIc(pyO), respectively. (b) Conversion of styrene leads to a mixture of epoxide, phenylacetaldehyde, and benzaldehyde (vide infra).

(28) Probably as a result of the catalytic rearrangement of styrene oxide via the coordinatively unsaturated chromium(III) product acting as a Lewis acid.

Table IV. Effects of Added Ligands on the Stoichiometric Oxidation of Styrene by Oxochromium(V)[a]

O=Cr^{V}L^{+}	added ligand (M)	% of styrene products[b] epoxide	PhCH$_2$CHO	PhCHO
IIb	none (0)[c]	8	29	7
	pyO (0.08)	78	11	6
	Et$_3$PO (0.08)	74	13	0
	Et$_3$PO (0.20)	77	19	1
IIf	none (0)[c]	31	59	2
	pyO (0.20)	57	27	19
	picO[d] (0.20)	49	4	44
	picO[d] (0.20)[e]	23[f]	h	31[g]
	Et$_3$PO(0.20)[e]	41[f]	h	5[g]

[a] In CH_3CN containing 0.02 M oxochromium(V) triflate and 0.20 M styrene, unless stated otherwise. [b] Based on oxochromium(V) charged, mol/mol conversion. [c] 1.0 m styrene. [d] 4-Picoline *N*-oxide. [e] 0.1 M *p*-nitrostyrene. [f] *p*-Nitrostyrene oxide. [g] *p*-Nitrobenzaldehyde. [h] Not determined.

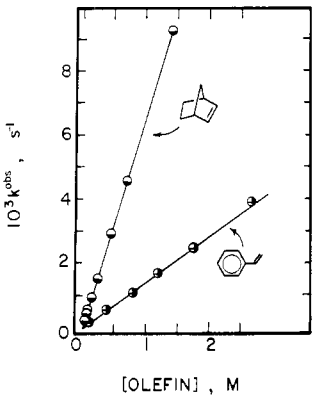


Figure 7. The first-order variation of the experimental rate constant k^{obsd} for the epoxidation with the oxochromium(V) cation IIb (0.0030 M) in CH_3CN containing 0.070 M triethylphosphine oxide and either (a) styrene or (b) norbornene.

dependent on the salen ligand as well as the donor ligand. Thus benzaldehyde is not a major product from the oxochromium(V) complex of tetramethylsalen IIb under any of the reaction conditions given in Table IV. By contrast, the dichloro analogue IIf affords benzaldehyde in 44% and 19% yields in the presence of picoline and pyridine *N*-oxides, respectively. Unlike pyridine *N*-oxide, triethylphosphine oxide did not enhance the yield of benzaldehyde.

V. Kinetics of Olefin Epoxidation with Oxochromium(V). The rates of olefin oxidation in acetonitrile were measured spectrophotometrically by observing the absorbance change of the oxochromium(V) adducts at λ_{max} (e.g., see Figure 4). The disappearance of oxochromium(V) followed clean first-order kinetics for more than 4 half-lives when suitably high concentrations of olefin and donor ligand D were present (vide infra). The pseudo-first-order rate constant (k^{obsd}) obtained under these conditions was independent of the initial concentration of oxochromium(V).

The effect of donor ligands on the rates was determined by measuring k^{obsd} for the epoxidation of norbornene with the oxochromium(V) species IIb at various concentrations of added D. In each case we observed the rate constant to reach limiting values which were unaffected by the further addition of the donor ligand, as shown in Figure 6. Such a kinetics saturation was also experimentally verified with other oxochromium(V) species and olefins. Since the concentration of the donor ligand necessary to produce the kinetics saturation is independent of olefin structure, the limiting behavior can be readily attributed to the reversible binding of the donor ligand to the oxochromium(V) center, as described by eq 5. Accordingly, the limiting value of the rate constant k_{∞}^{obsd} (see Figure 6) can be expressed as a second-order

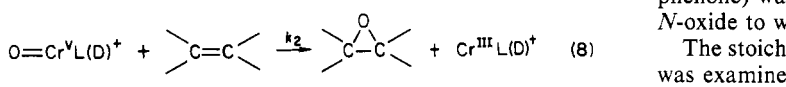
(29) For example, either styrene oxide or (*Z*)-β-methylstyrene oxide added to an active epoxidation consisting of 0.2 M norbornene, 0.02 M IIb, and 0.2 M pyridine oxide is quantitatively recovered intact (no phenylacetaldehyde).

Table V. Second-Order Rate Constants for Olefin Oxidation with Oxochromium(V) Complexes[a]

oxochromium(V) complex[b]	donor ligand[c] (M)	olefin (M)[d]	10^3k_2, M^{-1} s^{-1}
IIb	none	nb (0.1–0.8)	0.80
IIb	4-MepyO (0.32)	nb (0.1–0.8)	81
IIb	pyO (0.30)	nb (0.1–0.8)	77
IIb	Et_3PO (0.07)	nb (0.03–1.4)	66
IIb	Me_2SO (0.80)	nb (0.1–0.8)	46
IIf	pyO (0.30)	nb (0.1–0.6)	390
IIg	pyO (0.30)	nb (0.1–0.7)	37
IIh	pyO (0.35)	nb (0.1–0.8)	8.7
IIf	Et_3PO (0.07)	sty (0.1–1.8)	14
IIf	pyO (0.30)	4-MeO(sty) (0.05–0.2)	1400
IIf	pyO (0.30)	4-Me(sty) (0.1–0.5)	250
IIf	pyO (0.30)	sty (0.1–0.7)	90
IIf	pyO (0.30)	4-Cl(sty) (0.1–0.7)	80
IIf	4-MeOpy (0.30)	sty (0.1–0.5)	130
IIb	4-Me(py) (0.30)	sty (0.1–0.5)	110
IIf	pyO (0.30)	2-Me(sty) (0.1–0.5)	170
IIf	pyO (0.30)	2,6-Me(sty) (0.1–0.7)	12
IIf	pyO (0.30)	α-Me(sty) (0.1–0.3)	300
IIf	pyO (0.30)	E-β-Me(sty) (0.1–0.3)	160
IIf	pyO (0.30)	Z-β-Me(sty) (0.014[e])	110
IIf	pyO (0.30)	c-C_8H_{14} (0.2–0.5)	12

[a] In CH_3CN at 23 °C. [b] Initial concentration 3.0×10^{-3} M. [c] py = pyridine. [d] nb = norbornene, sty = styrene; concentration range in parentheses. [e] By competition, see Experimental Section.

rate constant k_2 by normalizing it with the concentration of the olefin present in excess, i.e., $k_2 = k_\alpha^{obsd}$ [olefin]$^{-1}$. Thus the values of k_2 represent the second-order reactions of the fully coordinated (see Figure 5) oxochromium(V) adduct with the olefin. In order to test this point, we examined the variation of k^{obsd} as a function of the olefin concentration in Figure 7.[30] The linear dependence of k^{obsd} on the concentrations of styrene and nonbornene supports the bimolecular process in eq 8 for oxygen atom transfer. The



(8)

validity of the formulation in eq 8 is quantitatively elaborated in the Discussion (see Scheme II and eq 16). [Note the lack of deviation from linearity in Figure 7, even at very high concentrations of norbornene (1.4 M) and styrene (2.6 M), provides no support for the kinetics saturation of k_2 by olefin.[31]]

The reactivities of olefins toward oxochromium(V) are listed in Table V according to the values of second-order rate constants k_2. The validity of the kinetics procedure described above was confirmed by an independent check with a competition method based on the disappearance of a pair of olefin (see Experimental Section). Thus the relative reactivity of 1.88 for α- and (E)-β-methylstyrene determined directly by the kinetics method was in accord with the value of 1.86 determined indirectly by the competition method.

Electronic effects on the oxygen atom transfer in eq 8 were examined by systematically replacing the substituent groups on (a) the 5,5′-positions of the salen complex, (b) the para position of the pyridine N-oxide as the donor ligand, and (c) the para position of styrene. The variations in the rate constant k_2 under the three sets of substituent changes are included in Table V.

VI. The Effects of Donor Ligands on the Rates and Products of Styrene Oxidation by Oxochromium(V). Owing to the variety of products derived from styrene in Table IV, we scrutinized its relationship to the rate of oxidation. The first-order rate constant

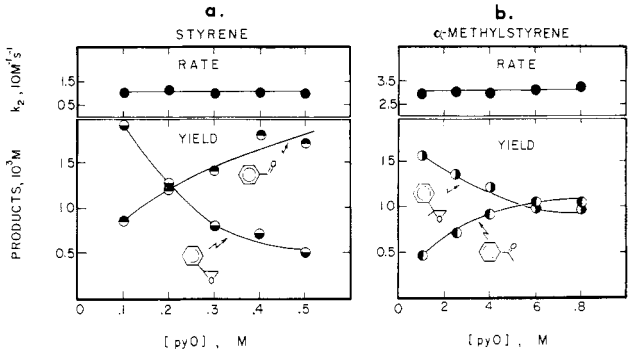


Figure 8. Effect of picoline N-oxide as the donor ligand in the oxidation of (a) 0.30 M styrene and (b) 0.10 M α-methylstyrene by the oxochromium(V) cation IIf (0.003 M) in acetonitrile. Upper: Variation of the rate constant k^{obsd}. Lower: Variation in the relative amounts of cleavage products and epoxides.

k^{obsd} was determined for the reaction of styrene with the oxochromium(V) species IIf at concentrations of 4-picoline N-oxide which were varied incrementally from 0.1 to 0.5 M. In this concentration range of the donor ligand, k^{obsd} has indeed reached its limiting value (viz., $k_\alpha^{obsd} = 3.3 \times 10^{-2}$ s^{-1}), as previously determined for norbornene in Figure 6. On the other hand, the quantitative analysis of the same reaction mixtures indicated a marked change in the complexion of the products. Thus the yield of styrene oxide is sharply diminished in the presence of picoline oxide and there is a concomitant increase in the benzaldehyde yield—which reached as high as 60% as shown in the lower half of Figure 8a.[32] Under the same conditions, the experimental rate constant k^{obsd} presented in the top of Figure 8a is strikingly invariant with increasing amounts of added donor ligand. Similarly, picoline N-oxide induces the oxidative cleavage of C=C bond in α-methylstyrene to acetophenone, although the effect is not as pronounced as that observed with styrene. In both cases, the combined yield of the epoxides and benzaldehyde (or acetophenone) was independent of the concentration of the pyridine N-oxide to within ±10%.

The stoichiometry for the carbon–carbon cleavage of styrene was examined by product analysis and oxygen-18 labeling experiments. Thus, the analysis of the reaction mixture derived from 0.2 M picoline N-oxide afforded a 39% yield of benzaldehyde and a 31% yield of picoline as the free base. In a separate experiment, formaldehyde (9%) was detected as both its phenylhydrazone and dimedone derivatives. The use of ^{18}O-labeled oxochromium(V) IIf indicated that 64% of the oxygen atom in benzaldehyde originated from the oxo function. Although the experimental limitations in the formaldehyde analyses preclude the establishment of a definitive stoichiometry,[33] the other results are consistent with the stoichiometry[34]

$$PhCH{=}CH_2 + O{=}Cr^VL^+ + 2picO \rightarrow PhCHO + CH_2O + 4\text{-}Me(py) + Cr^{III}L(picO)^+ \quad (9)$$

It must be emphasized that triethylphosphine oxide differs from either pyridine or picoline N-oxide in that it functions as the donor ligand without concomitantly inducing the oxidative cleavage of the C=C bond, as shown by the behavior of the substituted styrenes in Table VI. The incorporation of the isotopic oxygen from the ^{18}O-labeled oxochromium(V) into the various products is also included in Table VI.

Discussion

The rigorous identification of several key reactive intermediates offers us a rare opportunity to establish the catalytic mechanism

(30) The value of k^{obsd} at low olefin concentrations was obtained from the initial 10% of reaction.

(31) (a) Thus we could find no experimental evidence for the intervention of a pre-equilibrium step in eq 8. (b) However, in the *absence* of donor ligand the value of k_2 for IIb does decrease at [norbornene] > 0.75 M. Although this kinetics behavior may reflect a saturation phenomenon, we did not explore it further.

(32) (a) At these high concentrations of donor ligands, the yield of phenylacetaldehyde is insignificant (vide supra). (b) The total material balance for styrene oxidation varied from 93% to 76% at 0.1 and 0.5 M picoline oxide.

(33) The ready self-condensation of formaldehyde makes its quantitative analysis often difficult.

(34) The fate of the methylene groups missing in the analysis[33] could also lie as methylene complexes with chromium. Cf.: Fischer, E. O. *Adv. Organomet. Chem.* **1976**, *14*, 1.

Table VI. Ligand-Induced Cleavage of Olefins by Oxochromium(V); Isotopic ^{18}O Incorporation into the Products[a]

olefin (M)	ligand (M)	% yield of products[b] (% of O^{18} content[c]) ArCHC-H_2O	ArCHO	$ArCH_2C$-HO
Sty (0.20)	4-Me(py)O (0.20)	49 (100)	44 (63)	7 (*d*)
	Et_3PO (0.20)	77	1	20
	pyO (0.20)	57	19	27
4-Me(sty) (0.10)	4-Me(py)O (0.20)	22 (100)	41 (65)	9 (*d*)
	Et_3O (0.20)	81	2	20
2-Me(sty) (0.10)	4-Me(py)O (0.20)	26 (100)	28 (66)	4 (*d*)
	Et_3PO (0.20)	83	1	14
2,6-Me(sty) (0.10)	4-Me(py) (0.20)	64 (100)	6 (61)	*e*
	Et_3PO (0.20)	98	1	*e*
4-MeO(sty) (0.10)	4-Me(py)O (0.20)	*e*	65 (95)	19 (99)
	Et_3PO (0.20)	*e*	7	46
α-Me(sty) (0.10)	4-Me(py)O (0.20)	70 (96)	20 (100)[f]	12 (100)
E-β-Me(sty) (0.30)	4-Me(py)O (0.20)	96[g]	4	*e*
Z-β-Me(sty) (0.30)	4-Me(py)O (0.20)	54[h]	6	21[i]
Z-stilbene (0.30)	4-Me(py)O (0.20)	70[j]	4	

[a] With 2×10^{-2} M oxochromium(V) complex IIf in CH_3CN at 25 °C. [b] Based on oxochromium(V). [c] Normalized to ^{18}O content in IIf (80 ± 2%). [d] 100% but accuracy limited by low ion count. [e] Not determined. [f] Acetophenone. [g] *E* isomer, *Z* isomer too low to be determined. [h] *Z* isomer, plus 2% *E* isomer. [i] Benzyl methyl ketone. [j] (*Z*)-Stilbene oxide plus 5% *E* isomer.

of olefin epoxidation with terminal oxidants such as iodosylbenzene. As applied to the chromium(III) catalyst examined in this study, viz., $Cr^{III}(salen)^+$ (I), these intermediates are the coordinatively unsaturated oxochromium(V) species, $O{=}Cr^V(salen)^+$ (II), and its adduct with donor ligands D, $O{=}Cr^V(salen)(D)^+$ (III), both of which we have successfully isolated and structurally characterized, as shown by the ORTEP diagrams in Figures 3 and 5, respectively.

I. Mechanism of the Chromium(III)-Catalyzed Epoxidation of Olefins. Oxochromium(V) as the Reactive Intermediate. Knowledge of the reactivity and coordination chemistry of the various (salen)chromium complexes provides an unambiguous explanation for the otherwise puzzling, dichotomous behavior of pyridine *N*-oxide on the *rates* and *yields* in catalytic epoxidation, as initially noted in Figure 1. In particular, the maximum in the rate profile in Figure 1a can be dissected into two opposing effects of pyridine *N*-oxide as a donor ligand. On one hand, its coordination to the oxochromium(V) intermediate II in eq 5 affords an adduct III which is several orders of magnitude more reactive to oxygen atom transfer (see Figure 6). The steeply rising initial catalytic rate in Figure 1a is thus associated with the ligand coordination leading to enhanced oxochromium(V) reactivity. On the other hand, increasing concentrations of pyridine *N*-oxide can effectively tie up the chromium(III) catalyst as the octahedral complex $Cr^{III}(salen)(pyO)_2^+$,[35] thereby inhibiting the regeneration of the active oxochromium(V) species in eq 4. The sharply falling portion of the catalytic rate in Figure 1a thus derives from the inactivation of the chromium(III) catalyst.

The seminal role played by oxochromium(V) in the catalytic mechanism is also borne out in two other ways. First, the rather limited sensitivity of the epoxide yield to the presence of pyridine *N*-oxide in Figure 1b is readily accounted for by the observation that oxochromium(V) II and its adduct III are both capable of effecting epoxidation (see eq 6 and 7). Second, the products derived from the catalytic process are the same as those derived from the stoichiometric oxidation with oxochromium(V)—especially with regard to several unique byproducts and the particular stereochemistry of epoxide formation as revealed by a detailed comparison of the results in Tables I and III, respectively.

Scheme I

$$Cr^{III}L(D)^+ + PhIO \longrightarrow O{=}Cr^VL(D)^+ + PhI \quad (10)$$

$$O{=}Cr^VL(D)^+ + >C{=}C< \longrightarrow >C(O)C< + Cr^{III}L(D)^+ \quad (11)$$

Accordingly, the catalytic cycle is represented by an oxygen-rebound mechanism of the type originally proposed by Groves and co-workers.[3] The principal process for chromium(III) catalysis is summarized in Scheme I, where L is salen or its derivatives and D is pyridine *N*-oxide, triethylphosphine oxide, etc.

Both steps in the catalytic cycle in Scheme I may be strongly modulated by the donor ligand D as it affects the dynamics of ligand coordination to both chromium(III) and oxochromium(V) species. For example, three coordination complexes of (salen)-chromium(III) are extant at equilibrium, i.e.

$$Cr^{III}L^+ \overset{D}{\rightleftharpoons} Cr^{III}L(D)^+ \overset{D}{\rightleftharpoons} Cr^{III}L(D)_2^+ \quad (12)$$

The coordinatively saturated bis-ligand complex $Cr^{III}L(D)_2^+$ can be isolated (see eq 7), and it is inert to oxygen atom transfer from iodosylbenzene. Owing to the sparing solubility of iodosylbenzene, we were unable to measure its kinetics of oxygen atom transfer to either the 5-coordinate $Cr^{III}L(D)^+$ or the 4-coordinate $Cr^{III}L^+$. As a result, there is some ambiguity in the catalytic process as to whether the initial oxygen atom transfer occurs as in eq 10 or from the 4-coordinate species, i.e.

$$Cr^{III}L(D)^+ \rightleftharpoons D + Cr^{III}L^+ \xrightarrow{PhIO} O{=}Cr^VL^+, \text{ etc.} \quad (13)$$

Although the latter may be more reactive, the predominant species in the catalytic process is likely to be $Cr^{III}L(D)^+$ as a result of its formation in the subsequent step (see eq 11).[25] [Ligand dissociation is generally known to be relatively slow in chromium(III) complexes.[36]]

The oxochromium(V) cations are also affected by donor ligands, but only two coordination complexes of oxochromium(V) are extant at equilibrium as shown by the single isosbestic point in Figure 4, i.e.

$$O{=}Cr^VL^+ + D \rightleftharpoons O{=}Cr^VL(D)^+ \quad (14)$$

In the 5-coordinate cation, the Cr(V) center is displaced 0.53 Å above the salen plane. Figure 3 also shows the apical oxo function to be well poised for oxygen atom transfer to olefin, since it is accompanied by a concomitant retraction of the Cr(III) center back into the salen plane.[37] There are several features of ligand coordination to this coordinatively unsaturated complex which merits discussion. Thus the occupation of the sixth coordination site on the oxochromium(V) cation is subject to steric hindrance by peripheral substituents on salen. The latter probably arises from an increased strain which results from the Cr(V) center being pulled back toward (0.26 Å) the salen plane by axial ligation (Figure 5). Most importantly, axial ligation leads to the weakening of the O=Cr bond, which accounts for the increased reactivity of the 6-coordinate oxochromium(V) cation III relative to the coordinatively unsaturated percursor II.

The comparative reactivities of these oxochromium(V) species can be quantitatively evaluated by a kinetics procedure. Thus the variation of the rate of epoxidation with incremental changes in the concentration of the donor ligand in Figure 6 actually

(35) Salenchromium(III) affords adducts with two donor ligands, i.e., $(salen)Cr(D)_2$, see Experimental Section.

(36) Basolo, F.; Pearson, R. G. "Mechanisms of Inorganic Reactions", 2nd ed.; Wiley: New York, 1967; p 124ff.

(37) For example, the X-ray crystallographic determination of (salen)-$Cr(OH_2)_2^+Cl^-$ indicates the Cr(III) center to lie in the square plane formed by the pair of nitrogens and oxygens in salen.[38]

(38) Coggon, P.; McPhail, A. T.; Mabbs, F. E.; Richards, A.; Thornley, A. S. *J. Chem. Soc. A* **1970**, 3296.

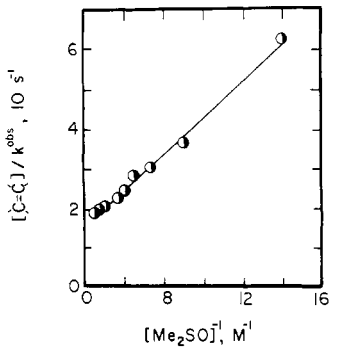
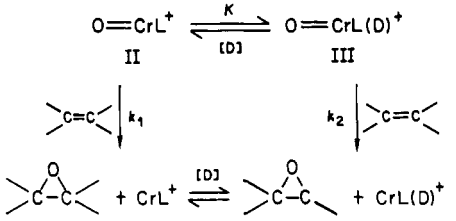


Figure 9. Combined kinetics for epoxidation with oxochromium(V) II and its donor adduct III according to eq 16 derived from Scheme II. [The data are taken from Figure 6 for Me_2SO as the donor ligand.]

Scheme II



reflects the relative reactivities of oxochromium(V) II and its adduct III, as outlined in Scheme II. In other words, the experimental rate constant k^{obsd} for epoxidation represents a composite of both processes. Since k^{obsd} is evaluated under pseudo-first-order rate conditions (i.e., with the olefin always present in excess), it can be expressed as

$$\frac{k^{obsd}}{[C{=}C]} = \frac{k_1 + k_2K[D]}{1 + K[D]} \qquad (15)$$

where k_1 and k_2 represent the second-order rate constants for olefin epoxidation by oxochromium(V) cation II and its donor adduct III, respectively, and K is the formation constant in eq 5. This formulation accords with the experimental observation described in Figure 6 that k^{obsd} reaches a constant limiting value (k_∞^{obsd}) at high concentrations of donor ligand D. At this limit the oxochromium(V) is effectively tied up as the adduct III, and it follows from eq 15 that $k_\infty^{obsd}/[C{=}C] = k_2$.[39] Coupled with the enhanced reactivity of the adduct III relative to II,[39b] eq 15 can be simplified to

$$[C{=}C]/k^{obsd} \simeq \frac{1}{k_2} + \frac{1}{k_2K[D]} \qquad (16)$$

The quantitative fit of the experimental rate data (see Figure 6) according to eq 16 is shown by the least-squares line in Figure 9, where the intercept is k_2^{-1} and the slope is $k_2^{-1}K^{-1}$. The value of $k_2 = 6 \times 10^{-2}$ M^{-1} s^{-1} obtained from the intercept Figure 9 is in complete accord with the value of $k_2 = 4.6 \times 10^{-2}$ M^{-1} s^{-1} measured directly at high concentrations of Me_2SO (see Table V). More importantly, the value of the formation constant K = 7 M^{-1} evaluated from the slope in Figure 9 is within experimental error of that (10 ± 1 M^{-1}) measured independently by spectral titration of the oxochromium(V) cation IIb.[40] We judge from the trend for k_2 in Table V that axial coordination of oxochromium(V) by donor ligand generally leads to enhanced reactivity by several orders of magnitude.[39b]

II. Mechanism of the Oxygen Atom Transfer from Oxochromium(V) to Olefins. Since we have identified the oxochromium(V) species as the crucial intermediate for the catalytic

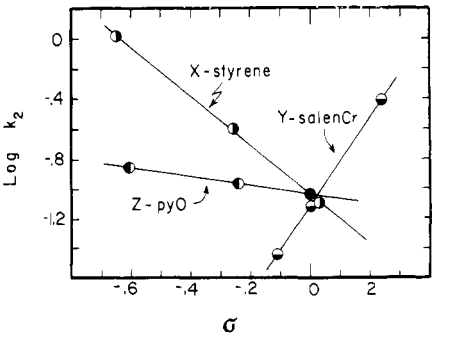
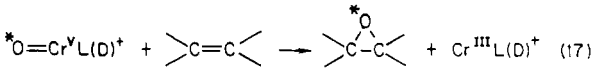


Figure 10. Substituent effects on the reactivity of a series of oxochromium(V) cations with various olefins. The Hammett correlation of (a) 4-substituted styrenes with oxochromium(V) cation IIf, using σ^+ constants, (b) norbornene with 5,5′-disubstituted oxochromium(V) cations IIb, IIf, and IIg, using σ constants, and (c) styrene with 4-substituted pyridine *N*-oxides and IIf, using σ_{pyO} constants.[41]

epoxidation in Scheme I, let us now consider how the oxygen atom is actually transferred from this species to the olefin in the rate-limiting step (eq 11).[8]

Isotopic ^{18}O labeling shows that epoxidation results from the transfer of the oxygen atom in the oxochromium(V) cation to the olefin substrate, i.e.



The absence of a kinetics saturation (even at the high concentrations of styrene and norbornene employed in Figure 7) indicates that in eq 17 a prior coordination of olefin to oxochromium(V), e.g., via a π-complex, is either absent or unimportant.

Three independent measures of reactivity point to the activated complex for oxygen atom transfer in eq 17 as one involving a strong component of electrophilic attack by the oxochromium(V) cation on the olefinic double bond. First, the trend in the second-order rate constants k_2 listed in Table VI demonstrates that electron-rich olefins such as norbornene and methylstyrenes are substantially more reactive than alkenes such as cyclooctene. The acyclic olefin hexene-2 and octene-1 react very slowly and afford epoxides in poor yields (cf. Table III). Moreover, the reactivities of a series of 4-substituted styrenes follow a Hammett correlation in Figure 10 with a ρ value of −1.9 when σ^+-substituent constants are used. Second, the presence of an electronegative substituent such as chlorine on the 5,5′-positions of salen (i.e., para to the oxygen center of salen) increases the reactivity of the oxochromium(V). Furthermore, the trio of substituted oxochromium(V) complexes IIb,f,g display an excellent Hammett correlation of log k_2 with σ (ρ = 2.9). Third, the series of 4-substituted pyridine *N*-oxides as the donor ligands do not induce large changes in the reactivity of the oxochromium(V) adduct III. However, the Hammett correlation in Figure 10 does accord with complexation to the cationic Cr center. [In the latter case, the substituent constants σ_{pyO} were derived from the Brønsted basicities of 4-substituted pyridine *N*-oxides.[41]]

Substituent effects on the olefinic substrate and the salen catalyst thus mutually support a rate-limiting transition state in which the oxochromium(V) functions as the electrophile. However, the electrophilic reactivity is attenuated, since the electron-rich aralkenes are strongly differentiated from the aliphatic olefins in the course of epoxidation. Substituent effects do not allow further delineation of the activated complex for oxygen atom transfer for oxochromium(V). In this regard the problem is as difficult as the extensive experimental and theoretical efforts expended in pinpointing the mechanism of olefin epoxidation with peroxides.[42]

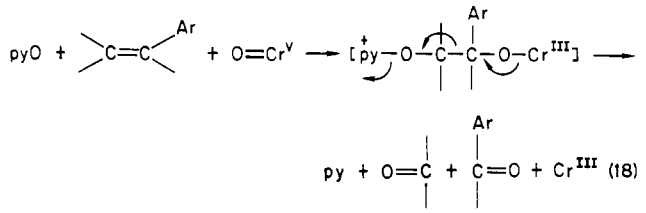
(39) (a) Figure 4 shows that at this limit, $K[D] \gg 1$. (b) Note that the cocatalytic effect of D is such that the adduct III is much more reactive than II, i.e., $k_2 > k_1$. Thus the second-order rate constant measured in the absence of Me_2SO (see Experimental Section) is 8.0×10^{-4} M^{-1} s^{-1}, whereas the limiting rate constant is 4.6×10^{-2} M^{-1} s^{-1} (see Table V). (c) Any oxidation of Me_2SO under these conditions is too slow to interfere.

(40) For the procedures, see ref 13.

(41) Nelson, J. H.; Garvey, R. G.; Ragsdale, R. O. *Coord. Chem. Rev.* **1968**, *3*, 375; *J. Heterocyclic Chem.* **1967**, *4*, 951.

(42) For a recent discussion of the mechanistic problem of delineating the transition state of oxygen atom transfer, see: Miyaura, N.; Kochi, J. K. *J. Am. Chem. Soc.* **983**, *105*, 2368.

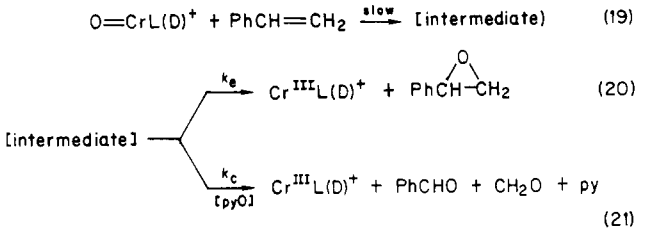
As limited as the substituent effects are in providing deeper insight, the byproducts of epoxidation do reveal an interesting entry into the mechanism of oxygen atom transfer from an alternative viewpoint. Thus two types of byproducts accompany epoxide formation with oxochromium(V); and they are especially notable with the styrenes, since the results in Table IV identify phenylacetaldehyde and benzaldehyde as important byproducts from styrene. Although some of the phenylacetaldehyde derives from the rearrangement of styrene oxide subsequent to its formation, a small but significant amount is actually formed during the epoxidation.[43] Likewise the traces of benzaldehyde become a major byproduct of epoxidation when either pyridine or picoline *N*-oxide (but not triethylphosphine oxide) is employed as the co-catalyst in relatively high concentrations (see eq 9). It is significant that the amount of benzaldehyde relative to styrene oxide increases as the amount of added pyridine *N*-oxide increases. Such an observation in Figure 8 (lower) indicates the occurrence of two competing processes—one leading directly to epoxide as in eq 8 and the other producing benzaldehyde by the C=C bond cleavage promoted by pyridine *N*-oxide, as in eq 9. The latter represents a 4-electron oxidation of styrene concomitant with the reduction of both oxochromium(V) and pyridine *N*-oxide. In order to facilitate recognition as such, it can be presented pictorially in the form



This *formal* representation does serve to underscore the inability of triethylphosphine oxide to promote C=C bond cleavage despite its properties as a donor ligand.[44]

It is important to note, however, that the pyO-promoted reaction proceeds without an attendant increase in rate. Thus the rate of oxochromium(V) disappearance in Figure 8 (upper) (i.e., the rate of olefin oxidation) varies by less than 10% under the same conditions that the relative rates of formation of epoxide and benzaldehyde are varying by more than a factor of 50. In other words, *the rate-limiting step for oxidation precedes and is separate from the product-forming step*. Such a kinetics situation can only arise if there are one or more intermediates which separate the reactants from the products in eq 11. The simplest mechanistic scheme to accommodate this conclusion includes one intermediate, as presented in Scheme III. According to Scheme III the intermediate which affords styrene oxide is diverted to benzaldehyde via a competing bimolecular attack by pyridine *N*-oxide in eq 21 (compare eq 9). This formulation predicts the mole fraction f_c of the cleavage product in Figure 8 (lower) to be given by the expression

Scheme III



$$f_c = \frac{[\mathrm{PhCHO}]}{[\mathrm{PhCHO}] + [\mathrm{PhCHCH_2O}]} = \frac{k_c[\mathrm{pyO}]}{k_c[\mathrm{pyO}] + k_e} \quad (22)$$

where k_e represents the first-order rate constant for epoxide formation and k_c is the second-order rate constant for cleavage. It follows from eq 22 that the reciprocal of the mole fraction f_c should be linear with the inverse of the donor concentration. The replotting of the data in Figure 8a indeed follows the expected linear relationship with $k_e = 0.24k_c$, as evaluated from the slope in Figure 11a. Thus at a unit molar concentration of the donor ligand, the transient intermediate is approximately 4 times more likely to undergo C=C cleavage to benzaldehyde than to afford styrene oxide.

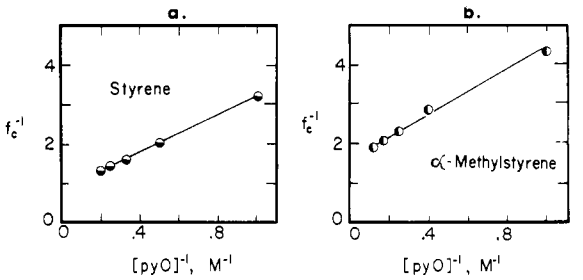


Figure 11. Kinetics derived from the partitioning of the common intermediate involved in the competition between epoxide formation and C=C cleavage of (a) styrene and (b) α-methylstyrene according to Scheme III.

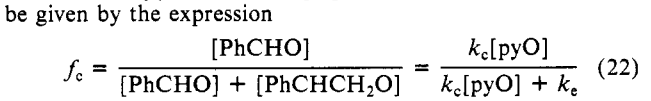
The validity of Scheme III to describe the competition between epoxide formation and C=C cleavage is supported by the same results obtained with α-methylstyrene oxidation. Thus Figure 11b shows that the reciprocal of the mole fraction of α-methylstyrene oxide is inversely related to the concentration of picoline oxide as predicted by a relationship equivalent to that in eq 22.[45]

The demonstration of an obligatory intermediate along the reaction coordinate for oxygen atom transfer in eq 11 by the combined use of a kinetics/products analysis does leave open the interesting question of its structure. Since this transient intermediate occurs after the rate-limiting oxygen atom transfer, the usual kinetics and isolation techniques are inapplicable. Therefore let us first consider whether the information inherent in the *competition* between epoxide formation and C=C cleavage in Scheme III can provide some structural insight. Any formulation of this intermediate must take into account the following factors.

i. Steric effects by methyl substituents on the α-, β-, and ortho-positions of styrene inhibit the C=C bond cleavage. For example, under comparable conditions the trend is for *o,o'*-dimethylstyrene, *o*-methylstyrene, and styrene to yield increasingly more benzaldehyde (6, 28, and 44%, respectively) as listed in Table VI. Similarly β-methylstyrene produces less than one-tenth as much benzaldehyde as styrene. The amount of cleavage of α-methylstyrene (20% acetophene) is less than half that observed with styrene. We conclude from these results that the interception of the intermediate by pyridine *N*-oxide in Scheme III is subject to steric retardation, as expected from a process involving a bimolecular attack.

ii. Isotopic ^{18}O-labeling studies identify the carbonyl oxygen in the cleavage product as arising either exclusively [e.g., 100% acetophenone-^{18}O from α-methylstyrene and 95% anisaldehyde-^{18}O from *p*-methoxystyrene]

or predominantly [e.g., 63% benzaldehyde-O^{18} from styrene, 65% p-tolualdehyde-O^{18} from p-methylstyrene, 66% o-tolualdehyde-O^{18} from o-methylstyrene and 61% 2,6-dimethylbenzaldehyde-O^{18} from 2,6-dimethylstyrene] from the ^{18}O-labeled oxochromium(V) cation IIf, as given in Table VI.

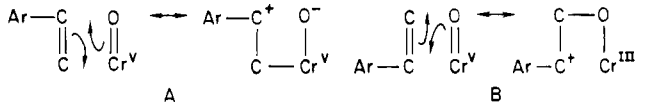


(43) See Experimental Section for details.

(44) Although amine oxides can be considered as oxidants (see ref 1), the scission of the O–P bonds in phosphine oxides is difficult.

(45) It should be noted, however, that the line in Figure 11a does not extrapolate to 1, as predicted by eq 22. In other words, there is an additional minor route to α-methylstyrene oxide which either involves a direct bimolecular process or one dependent on D.

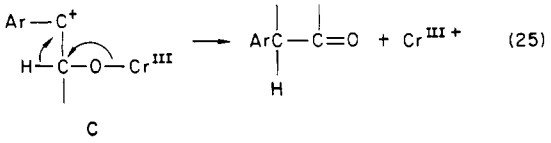
Control experiments have rigorously ruled out any exchange process (e.g., with adventitious water) as the source of isotopic dilution in the latter cases[46] (see Experimental Section). Therefore, the ^{18}O-tracer studies indicate that the regioselectivity in the C=C cleavage is dependent on the olefin structure. In *p*-methoxy- and α-methylstyrene, the exclusive benzylic attack by oxochromium(V) leading to C=C cleavage accords with their ability to stabilize positive charge at this position. A partial representation consistent with this conclusion can be depicted as A. However, in the absence of such a strong polarizing influence, the α- and β-carbon in the other styrenes are not strongly differentiated, which is brought out by the incursion of the other regioisomer B.



A B

iii. Stereochemistry of epoxide formation indicates predominant, but not exclusive, retention of configuration at the trigonal carbon centers. *trans*-Olefins such as (*E*)-β-methylstyrene, (*E*)-stilbene, and (*E*)-hexene-2 proceed with >99% retention to afford the corresponding (*E*)-epoxides (see Tables I and III). The epoxidation of *cis*-olefins affords variable amounts of the rearranged (*E*)-epoxides, which vary from ~2% with (*Z*)-β-methylstyrene and (*Z*)-stilbene to ~10% from (*Z*)-hexene-2. These results are reminiscent of driving forces for rearrangement of cisoid configurations in olefins and epoxides which are greater than those of their transoid counterparts. Accordingly we interpret the high, but not complete, retention of stereochemistry to auger a short-lived intermediate in which the C=C bond is sufficiently opened to allow some rotation. [Note the olefin is always recovered unrearranged.]

iv. Skeletal rearrangement of the olefinic moiety is inherent to the oxidation with oxochromium(V). It is reported in Table VI as the minor (~10%) byproducts phenylacetaldehyde from styrene, (*o*- and *p*-methylphenyl)acetaldehyde from *o*- and *p*-methylstyrene, α-phenylpropionaldehyde from α-methylstyrene, and benzyl methyl ketone from (*Z*)-β-methylstyrene. By contrast, (*p*-methoxyphenyl)acetaldehyde is the major product (>60%)[47] from *p*-methoxystyrene, and insignificant amounts (<1%) of rearrangement products are derived from either the sterically hindered *o*,*o*'-dimethylstyrene or the *E* isomer of β-methylstyrene. The nature of the products and substituent effect are consistent with a cationic rearrangement. Furthermore, isotopic ^{18}O labeling proves the carbonyl oxygen in the rearrangement product to derive exclusively from the oxochromium(V) function (see Table VI). These observations suggest a partial structure for the intermediate of the following type:[48]

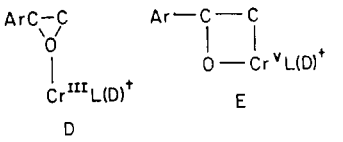


C (25)

The marked differentiation between the (*E*)- and (*Z*)-β-methylstyrenes indicates a conformational requirement for the hydrogen rearrangement, which is suggestive of a partially closed (i.e., cyclic) structure, as in B.

v. Substituent effects in the C=C cleavage are manifested in two ways. First, the electron-withdrawing chlorine substituents on the 5,5'-position of salen in IIf promote C=C cleavage substantially over that of the unsubstituted IIb (see Table IV). Second, the presence of the electron-releasing, *p*-methoxy group on styrene facilitates C=C cleavage. Such a mutual reinforcement of polar substituents is also consistent with the partial formulation in eq 25.

When the mechanistic probes in i–v are taken all together, they do not offer a compelling case for a single discrete structure to describe the intermediate. However, they do point a quasiclosed species with positive charge on the benzylic center. Thus if we are forced to choose a single intermediate, the closest representative would be either D or E. In these structures, the O–C_α bond must



D E

be sufficiently polarized (i.e., $O^-C_\alpha{}^+$) to allow (a) limited rotation around the C_α–C_β bond, (b) Wagner–Meerwein rearrangement, and (c) nucleophilic attack by pyridine *N*-oxide. Structure E which was previously presented speculatively by Sharpless and co-workers,[49] suffers from a hypervalent 7-coordinate chromium center. This difficulty may, however, be accommodated by breaking one of the nitrogen bonds to Cr. Structure D is a close relative to the activated complex based on the concept of least motion[50] for the rate-limiting step. As such, it corresponds to the inner-sphere complex of the epoxide and the chromium(III) product. Attempts at an independent synthesis of D from epoxide and the 5-coordinate $Cr^{III}L(D)^+$ indeed afforded benzaldehyde among other products (see Experimental Section). Owing to their close similarity, the further differentiation of structures D and E was not pursued.

Experimental Section

Materials. Styrene, *p*-methoxy-, *p*-methyl-, and *p*-chlorostyrene, norbornene, α- and (*Z*)-β-methylstyrene, cyclooctene, cyclohexene, and (*E*)- and (*Z*)-stilbene were commercial samples from Aldrich. *o*-Methyl- and *o*,*o*'-dimethylstyrene (Fairfield Research Chemicals) and (*E*)- and (*Z*)-hexene-2 (Wiley) were also commercial samples. 4-Cyano- and 4-nitrostyrene were prepared by literature methods.[51] All the olefins were repurified by fractional distillation from either sodium or lithium aluminum hydride when feasible. The exceptions were (*E*)- and (*Z*)-stilbenes which were chromatographed on alumina and 4-nitrostyrene which was recrystallized from methanol at −40 °C.[52] The purified olefins were stored in evacuated ampules at −20 °C, except the styrenes which were stored at −78 °C. Prior to use, the olefins were passed over alumina, and all subsequent manipulations were conducted under either an argon or a nitrogen atmosphere with use of standard Schlenkware or glovebox techniques. Each of the olefins was converted to its epoxide with *m*-chloroperbenzoic acid with use of the conventional procedure.[53]

The various salenH_2 analogues as Schiff base adducts were prepared from ethylenediamine and the corresponding salicyaldehydes (Aldrich) by standard methods.[54] 2,3-Diaminobutane was prepared from 2-nitropropane according to Sayre's procedure.[55] Isodosylbenzene was prepared from iodobenzene diacetate (Aldrich) according to the literature method.[56] Pyridine and 4-picoline *N*-oxide were obtained from Aldrich. 4-Methoxypyridine oxide was synthesized according to Ochiai.[57] Triethylphosphine oxide was prepared by the oxidation of triethylphosphine with N_2O.[58] Each of these hygroscopic compounds was sublimed in vacuo and stored in a Vacuum Atmosphere glovebox. All subsequent manipulations utilized aliquots of standard stock solutions in acetonitrile which was prepared and stored under airless conditions. Acetonitrile and dimethyl sulfoxide (Fisher reagent grade) were first refluxed over calcium

(46) The concomitant formation of pyridine suggests that the unlabeled benzaldehyde derives from py^{16}O. Unfortunately the unavailability of py^{18}O has not allowed us to prove this point.

(47) The facile rearrangement of *p*-methoxystyrene oxide did not allow us to make a rigorous distinction.

(48) Similar cationic intermediates have been suggested by Groves and Myers[4b] to account for the same rearrangement with oxoiron porphyrins.

(49) Sharpless, K. B.; Teranishi, A. Y.; Backvall, J. E. *J. Am. Chem. Soc.* **1977**, *99*, 3120.

(50) (a) Rice, F. O.; Teller, E. *J. Chem. Phys.* **1938**, *6*, 489. (b) Hine, J. *Adv. Phys. Org. Chem.* **1977**, *15*, 1.

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(53) Swern, D. *Org. React.* **1953**, *7*, 378.

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(55) Sayre, R. *J. Am. Chem. Soc.* **1955**, *77*, 6690.

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(57) Ochiai, E. *J. Org. Chem.* **1953**, *18*, 534.

(58) Staudinger, H.; Hauzer, E. *Helv. Chim. Acta* **1921**, *4*, 861.

hydride and then distilled under argon. They were stored in Schlenk vessels fitted with greaseless Teflon stopcocks.

Preparation of (salen)Cr^{III} Cationic Complexes. The salenchromium(III) complex Ib was prepared by addition of chromous triflate (3.5 g in 20 mL of acetone) dropwise to a suspension of 2.5 g (7.7 mmol) of 8,8,8′,8′-Me$_4$salenH$_2$ in 100 mL of acetone under argon. The reaction mixture turned brown, and the color change was accompanied by the dissolution of the ligand. After being stirred for 30 min, the reaction mixture was exposed to air and stirred for an additional hour. Water (30 mL) was added, and after being stirred for 15 min the mixture was concentrated in vacuo to ~60 mL. The salenchromium(III) complex was isolated by filtration as a deep yellow solid. It was washed with deionized water twice and dried in air to afford 2.8 g (5.0 mmol, 65%) of Ib: IR (Nujol) 3300–3600, 2800, 1617, 1603, 1552, 1474, 1447, 1400, 1285, 1240, 1224, 1174, 1160, 1145, 1127, 1027, 960, 908, 881, 844, 797, 754, 639 cm^{-1}; UV–vis (CH$_3$CN) 418 nm (ϵ 4780), 360 (8112) (sh), 316 (1.6×10^4) (sh), 286 (2.5×10^4), 208 (6.8×10^4); magnetic susceptiblity (CH$_3$CN) μ_{eff} 3.80 μ_B.[15b] The complexes Ia and Ic–h were prepared and characterized in a similar manner.[13]

Preparation of Oxochromium(V) Cationic Complexes. The oxochromium(V) salt IIb was prepared from 0.60 g (1.1 mmol) of the salenchromium(III) salt Ib in 25 mL of acetonitrile with 0.28 g (1.27 mmol) of iodosylbenzene. The suspension was stirred for 30 min, and the dark brown-black solution was filtered to remove unreacted iodosylbenzene. Anhydrous ether (50 mL) was added, and the oxochromium(V) complex was isolated as a flaky black solid by filtration. Yield 0.36 g (0.67 mmol, 62%) of IIb: IR (Nujol) 2800, 1600, 1593, 1463, 1453, 1396, 1378, 1272, 1259, 1226, 1030, 1002, 907, 853, 811, 744 cm^{-1}; UV–vis (CH$_3$CN), see Figure 2; magnetic susceptibility (CH$_3$CN) μ_{eff} 1.76 μ_B.[15b]

The isotopic ^{18}O derivative was synthesized from 0.60 g (0.97 mmol) of IIb in 150 mL of acetonitrile and 2.0 g of H$_2$O^{18} (90% isotopic enrichment from Aldrich). The resulting light green solution was stirred at room temperature for 24 h under an argon atmosphere. Addition of Linde 4A molecular sieve to the solution changed the color from green to brown-black indicative of the removal of coordinated water. The solution was filtered and concentrated to 40 mL in vacuo. Freshly distilled anhydrous ether (100 mL) was added and the black precipitate collected by filtration. Yield 0.37 g (0.59 mmol, 60%). The comparison of the IR bands at 1004 and 965 cm^{-1} for the ^{16}O=Cr and ^{18}O=Cr stretching bands indicated an ~80% enrichment.

Preparation of the Donor Adduct to Oxochromium(V). The donor adducts III to oxochromium(V) were generally prepared in situ by adding an excess of the stock solution of the donor ligand D (vide supra) to solutions of II—which resulted in an immediate color change from dark brown-black to emerald green. However, the analogue IIIf (D = pyridine *N*-oxide) was isolated as a single crystal as follows. To a solution of 0.014 M IIf and 0.2 M pyridine *N*-oxide in 6 mL of CH$_2$Cl$_2$ contained in a Pyrex tube sealed with an air-tight rubber septum at −20 °C was carefully added 10 mL of hexane as a separate layer. Partial diffusion occurred over 3 days at −20 °C to afford a small crop of large dark green needles. The IR spectrum of IIIf showed a characteristic band at 943 cm^{-1}. The X-ray crystallography is described separately.[13]

Instrumentation. The electronic absorption spectra were measured with a Hewlett-Packard Model 8450A diode array spectrometer with a 0.1 s time resolution. The X-band ESR spectra were recorded on a Varian Century-line Model E-112 spectrometer with a NMR gaussmeter for field-frequency calibration. Magnetic susceptibility was measured at 25 °C by the Evans' method in acetonitrile solution with a JEOL Model FX-90Q NMR spectrometer.[15] Infrared spectra were obtained either on a Beckmann Model 1330 (dispersion) or a Nicolet Model DX-10 (fourier transform) spectrometer. Organic analyses were conducted on either a Hewlett-Packard 5790 or 5890 gas chromatograph fitted with either a 12.5-m cross-linked dimethylsilicone or a 30-m carbowax capillary column. The analysis of the stilbene oxides and (*p*-methoxyphenyl)acetaldehyde were carried out with cool on-column techniques. Quantification of the product was determined by the internal standard method with chlorobenzene, *n*-decane, or *n*-undecane. The identity of each product was confirmed by independent synthesis and comparison of the mass spectral cracking pattern from a Hewlett-Packard Model 5790B mass spectrometer interfaced to the Model 5890 gas chromatograph.

Procedure for Catalytic Epoxidation with Salenchromium(III). A typical procedure for the catalytic epoxidation of olefins was carried out with 12 mg (0.055 mmol) of iodosylbenzene suspended in a solution consisting of 1.1–1.3 mmol of olefin, 0.011 mmol of salenchromium(III) complex Ib, 0.006 mmol of pyridine *N*-oxide (added as 5 μL of a 1.2 M solution in CH$_3$CN), and an internal standard (either chlorobenzene or *n*-decane) in 1 mL of acetonitrile which was sealed under argon. The suspension was stirred magnetically until all the suspended iodosylbenzene disappeared. Gas chromatographic analysis was performed on aliquots which were withdrawn periodically from the reaction mixture with the aid of a hypodermic syringe.

Procedure for the Stoichiometric Epoxidation with Oxochromium(V). To a solution of 0.020 mmol of oxochromium(V) IIb in 1 mL of acetonitrile contained in a Schenk flask under argon was added 0.08 mmol of pyridine *N*-oxide (48 μL of a 1.67 M stock solution) and 0.025 mmol of decane. After 0.5 h, gas chromatographic analysis indicated the presence of 0.016 mmol (78%) of styrene oxide, 0.0021 mmol (11%) of phenylacetaldehyde, and 0.0012 mmol (6%) of benzaldehyde. Control experiments established the following: (a) styrene oxide is stable to the reaction conditions, i.e., inclusion of the epoxide to a reaction of IIb and pyridine *N*-oxide with norbornene resulted in no detectable consumption or rearrangement of styrene oxide; (b) styrene oxide does not rearrange upon gas chromatographic injection if the injection liner and silanized glasswool are clean; and (c) introduction of the alkane internal standard before or after the reaction affords the same analytical results.

Determination of the Stoichiometry for Stoichiometric Epoxidation. To 11.2 mg (0.021 mmol) of oxochromium(V) IIb in 0.75 mL of acetonitrile was added 0.20 mmol of triethylphosphine oxide (0.21 mL of 0.94 M stock solution), *n*-octane and *n*-decane as internal standards, and 0.040 mmol of norbornene. Analysis after 70 min indicated that 0.88 equiv of norbornene was consumed and 0.94 equiv or norbornene oxide was formed. The chromium containing product was isolated from a similar reaction mixture by removing the solvent in vacuo. The residual red oil solidified upon stirring with 10 mL of hexane to give 0.17 mmol (90%) of bis(triethylphosphine oxide)(8,8,8′,8′-tetramethylsalen)chromium(III) (trifluoromethane)sulfonate: IR (KBr) 2960, 1601, 1530, 1470, 1440, 1395, 1335, 1310, 1255, 1215, 1140, 1120, 1090, 1025, 905, 840, 880-850, 630, 610, 525, 460, cm^{-1}. Anal. Calcd for C$_{33}$H$_{52}$F$_3$N$_2$O$_7$P$_1$SCr: C, 49.92; H, 6.48; N, 3.60. Found: C, 49.47; H, 6.80; N, 3.11. This complex was independently prepared by refluxing 0.43 g (0.77 mmol) of diaquo(tetramethylsalen)chromium(III) triflate Ib with 0.45 g (3.25 mmol) of triethylphosphine oxide in 40 mL of benzene for 2 h. Upon cooling a red oil precipitated which was reprecipitated from a mixture of CH$_2$Cl$_2$ and hexane to afford 0.52 g (86%) of a red solid which had the same IR spectrum as that reported above. The chromium-containing product isolated from a reaction in the absence of added donor ligand was isolated from 102 mg of IIb in 10 mL of CH$_3$CN containing 941 mg of norbornene. After 4 h, 1 mL of water was added and the solution evaporated to dryness in vacuo. The IR spectrum of the orange solid isolated in 98% yield was the same as that of Ib.

Determination of the Kinetics of Oxochromium(V) Epoxidation. The pseudo-first-order rate constant k^{obsd} was determined from the plot of $-\ln(A - A_\infty)$ against time, where A is the absorbance at λ_{max} (~650 for III, see Figure 4) and A_∞ is the experimentally determined infinity point. These plots were linear over more than 4 half-lives. An exception involved those runs in the absence of donor ligands for which the rate was determined from the disappearance of IIb (at 650 nm, ϵ 893 M^{-1} cm^{-1}) within the first 10% of reaction; the slope of the line was divided by the median value of IIb to give approximate values of k^{obsd}.

Second-order rate constants were determined as the least-squares slopes of the plots of k^{obsd} vs. [olefin], under conditions in which the concentration of added donor ligand was held constant at values greater than necessary to produce kinetics saturation (see Figure 6). A typical example was obtained in a Schlenk cuvette (1.0 mm path length) to which a solution containing 0.0030 mmol of IIb and 0.300 mmol of pyridine *N*-oxide in 0.56 mL of CH$_3$CN was added. To the sidearm reservoir was placed a solution containing 0.75 mmol of norbornene in 0.44 mL of CH$_3$CN. The absorbance, which was recorded at 4-s intervals after mixing, reached a constant value of 0.019 after ~2 min. The least-squares analysis through 48 s afforded $k^{obsd} = 5.78 \times 10^{-2}$ s^{-1} with a correlation coefficient of 0.999.

The kinetics runs, in which the ligand concentration was varied, were conducted by a slightly different procedure. Typically, to a Schlenk cuvette was added 0.50 mL of a stock solution containing 0.0030 mmol of IIb and 0.30 mmol of freshly distilled Me$_2$SO and 0.42 mL of CH$_3$CN. The kinetics run was carried out with a stock solution of norbornene in the sidearm as described above. Repetition of the experiment at higher concentrations of Me$_2$SO was offset by smaller amounts of CH$_3$CN to maintain the total volume to 1 mL. All kinetics determinations were monitored by following the absorbance change at λ_{max}, which was 630 nm for IIb(pyO), 630 nm for IIb(picO), 650 nm for IIf(picO), 650 nm for IIf(4MeOpy), 646 nm for IIb(Et$_3$PO), and 626 for IIb(Me$_2$SO).

Relative Reactivities by Intermolecular Competition. Into a Schlenk flask was placed a mixture of 0.032 mmol of (*Z*)-β-methylstyrene and 0.034 mmol of (*E*)-β-methylstyrene and 0.30 mmol of pyO, decane, and undecane as internal standards under argon. The addition of 0.023 mmol of IIf was carried out with an argon flush. After 20 min, the orange solution was analyzed by gas chromatography to afford 0.023 mmol of

Table VII. Rates and Products of Oxidation of α-Methylstyrene with Oxochromium(V)[a]

[picO], M	$10^2 k^{obsd}$, s^{-1}	$PhC(CH_3)$-CH_2O,[b] 10^5 M	$PhC(CH_3)O$,[b] 10^5 M	$PhCH(CH_3)$-CHO,[b] 10^5 M
0.10	2.96	157 (5)	47 (2)	55 (3)
0.25	3.03	135 (5)	72 (2)	34 (4)
0.40	3.00	122 (8)	92 (3)	*c*
0.60	3.17	106 (2)	98 (1)	*c*
0.80	3.17	97 (3)	103 (3)	*c*

[a] From 3.0×10^{-3} mmol IIf, 0.10 mmol α-methylstyrene, and added donor (picO) as stated in 1 mL of CH_3CN at 25 °C. [b] Numbers in parentheses are standard deviation in the last significant digit from the average of >4 injections. [c] Too low to measure.

(*Z*)-β-methylstyrene, 0.020 mmol of (*E*)-β-methylstyrene, 0.0059 mmol (26%) of (*Z*)-epoxide, 0.013 mmol (57%) of (*E*)-epoxide, and 0.0032 mmol (14%) of benzyl methyl ketone. Thus the consumption 0.014 mmol (*E*)-olefin and 0.0092 mmol of (*Z*)-olefin gives the ratio $k_2(E)/k_2(Z) = 1.44 = \Delta EZ_0/\Delta ZE_0$. This method was checked with α-methylstyrene and (*E*)-β-methylstyrene which gave the rate constant ratio $k_2(\alpha)/k_2(E) = 1.86$ in accord with the value 1.88 obtained from the values of k_2 in Table V.

Isotopic ^{18}O-Labeling Studies of Oxochromium(V). Oxochromium(V) IIf-^{18}O was prepared by exchange of IIb with $^{18}OH_2$ as described elsewhere.[13] The isotopic distributions in the organic products were determined by GC–MS analysis by comparing the ion counts for the parent molecular ion $M(^{16}O)^+$ and $M(^{18}O)^+$ in the epoxide and the rearranged and the cleaved carbonyl compounds. In every case the mass spectrum was not complicated by the presence of M + 2 or M − 2 ions. However, owing to the low abundance of the molecular ion in α-methylstyrene, it was analyzed by measuring the *m/e* 29 and 31 (CHO^+) peaks.

It was shown that picoline *N*-oxide does not dilute the oxygen label in the following way. Norbornene with IIf (with 60% ^{18}O enrichment) gave norbornene oxide with 59% ^{18}O enrichment. The same experiment with 5 equiv of added picoline oxide afforded norbornene oxide with the same (63%) ^{18}O enrichment. Examination of the picoline oxide peak revealed no ion at *m/e* 111 for $M(^{18}O)^+$. The oxidation of styrene with IIf (80% ^{18}O enrichment) and 10 equiv of picoline oxide afforded styrene oxide with 80% ^{18}O enrichment. However, the accompanying benzaldehyde showed 51% enrichment which corresponds to 63% of the oxygen originating for the oxo complex. The control experiments to establish whether adventitious exchange occurred under reaction conditions were carried out in the following way. Oxochromium(V) IIf (80% ^{18}O enriched), picoline *N*-oxide, and styrene in acetonitrile were treated with 5 equiv of either H_2O^{16} or H_2O^{18}; the styrene oxide was found to contain 71% and 86% ^{18}O enrichment, respectively, whereas the benzaldehyde consisted of 46% and 50% ^{18}O enrichment, respectively. These results are consistent with an ^{16}O–^{18}O exchange in the oxochromium(V) complex prior to reaction,[13] rather than exchange with benzaldehyde subsequent to its formation.

Oxidative Cleavage of Styrenes with Oxochromium(V). To 0.020 mmol of IIf and 0.20 mmol of 4-picoline *N*-oxide in 1.0 mL of CH_3CN was added 0.20 mmol of styrene. After completion of the reaction, gas-chromatographic analysis indicated the presence of 0.0062 mmol (31%) of 4-picoline, 0.0078 mmol (39%) of benzaldehyde, and 0.0064 mmol (32%) of styrene oxide. In an identical experiment, 0.10 mmol of phenylhydrazine was added prior to analysis and 0.0018 mmol (9%) of formaldehyde hydrazone and 0.0089 mmol (44%) of benzaldehyde hydrazone were detected. The identity of both hydrazones was confirmed by comparison of the GC–MS with that of the authentic material.

The stability of styrene oxide under reaction conditions was established with the following controls. To 0.020 mmol of IIf and 0.20 mmol of picoline oxide in 1 mL of CH_3CN was added 0.030 mmol of styrene oxide. After the mixture was stirred for 10 min (which was larger than a typical reaction time), analysis indicated only traces of benzaldehyde and no phenylacetaldehyde. Styrene oxide was recovered intact (0.029 mmol). Alternatively, 0.020 mmol of IIf and 0.020 mmol of picoline oxide was treated with 0.20 mmol of norbornene. Upon reduction to chromium(III) (~10 min), as indicated by the color change to orange, 0.030 mmol of styrene oxide was added. After the mixture was left to stand for 25 min, analysis indicated the presence of 0.027 mmol of styrene oxide, 0.0014 mmol (7% rel. Cr) of phenylacetaldehyde, and 0.000 30 mmol (1%) of benzaldehyde. Next, to a solution containing 0.014 mmol of styrene oxide and 0.0024 mmol of phenylacetaldehyde, 0.020 mL of 4-chlorostyrene, and 0.20 mmol of picoline oxide was added 0.020 mmol of IIf. Subsequent to reaction, analysis indicated the presence of 0.0024 mmol of phenylacetaldehyde and 0.012 mmol of styrene oxide in addition to 4-chlorobenzaldehyde, 4-chlorostyrene, and its epoxide. The equivalent experiment was carried out with 0.114 mmol of α-methylstyrene oxide and 0.0036 mmol of 2-phenylpropionaldehyde in place of styrene oxide and phenylpropionaldehyde. After completion of the reaction, 0.0109 mmol of the residual epoxide and 0.0046 mmol of the aldehyde were recovered. Acetophenone was not detected (<1%). However, extensive oxidation of 4-chlorostyrene to 4-chlorobenzaldehyde was noted.

The relationship between the rate and products of oxidation as a function of the donor concentration was carried out in the following manner. To a 1.0-mm Schlenk cuvette was added 0.0030 mmol of IIf and 0.40 mmol of picoline oxide in 1 mL of CH_3CN. α-Methylstyrene (0.10 mmol) was stored in the sidearm. Upon mixing the absorbance change at 650 nm was automatically monitored at 10-s intervals for 110 s. The infinity absorbance ($A_\infty = 0.013$) was reached within 20 min. The least-squares rate constant (determined as described above) was 3.00×10^{-2} s^{-1}. The resultant solution was analyzed directly by gas chromatography to contain 0.0012 ± 0.0008 mmol (40 ± 3%) of α-methylstyrene oxide and 0.00092 ± 0.00003 mmol (30 ± 1%) of acetophenone in addition to 2-phenylpropionaldehyde in small amounts. Subsequent runs with different amounts of donor were carried out in the same way by adjusting the volume of CH_3CN to always maintain a total of 1 mL of solution. A typical result is shown in Table VII. Analogous reactions with styrene (Figure 8a) were carried out similarly to afford picO(M), styrene oxide (%), benzaldehyde (%) as 0.10, 64 ± 3, 29 ± 2; 0.20, 42 ± 1, 39 ± 9; 0.30, 28 ± 4, 48 ± 3; 0.40, 24 ± 2, 60 ± 9; 0.50, 19 ± 3, 57 ± 1.

The instability of styrene oxide in the absence of added donor ligand was shown by taking 0.020 mmol of IIf and 0.20 mmol of norbornene in 1 mL of CH_3CN. After completion of the oxidation (~10 min), 0.030 mmol of styrene oxide was added and the solution stirred for 20 min. Analysis indicated the presence of 0.013 mmol of styrene oxide, 0.0089 mmol of phenylacetaldehyde, and 0.0038 mmol of benzaldehyde. However, if 0.20 mmol of picoline oxide was added to the reaction mixture prior to gas chromatographic analysis, 0.024 mmol of styrene oxide, 0.0034 mmol of phenylacetaldehyde, and 0.0033 mmol of benzaldehyde were formed. Thus the mass balance was increased from 0.023 to 0.031 mmol upon the addition of ligand. An equivalent experiment was conducted in which 0.030 mmol of styrene oxide was stirred for prolonged periods with the "bare" chromium(III) product with no added donor ligand. After 12 h, the solution contained no styrene oxide, 0.010 mmol of phenylacetaldehyde, and 0.015 mmol of benzaldehyde.

Acknowledgment. We thank J. D. Korp for the crystallographic structures in Figures 3 and 5, the National Science Foundation, and the R. A. Welch Foundation for financial support.

Registry No. Ia, 98736-54-0; Ib, 98736-56-2; Ic, 98736-58-4; Id, 98736-60-8; Ie, 98736-62-0; If, 98736-64-2; Ig, 98736-66-4; Ih, 98736-68-6; IIa, 98736-73-3; IIb, 98736-75-5; IIb (picO), 98736-82-4; IIb (Et_3O), 98736-85-7; IIb (Me_2SO), 98736-86-8; IIc, 98736-77-7; IId, 98736-72-2; IIe, 98736-79-9; IIf, 98736-81-3; IIf (picO), 98736-83-5; IIf (4MeOpy), 98736-84-6; IIIb, 98736-69-7; IIIf, 98736-70-0; 4-MeOsty, 637-69-4; 4-*Mesty*, 622-97-9; 4-Clsty, 1073-67-2; 4-MeOpy, 620-08-6; 2-Mesty, 611-15-4; 2,6-Me_2sty, 2039-90-9; α-Mesty, 98-83-9; PhIO, 536-80-1; Me_2SO, 67-68-5; PhCHO, 100-52-7; $PhCH_2CHO$, 122-78-1; 4-$MeC_6H_4CHCH_2O$, 13107-39-6; 4-MeC_6H_4CHO, 104-87-0; 4-$MeC_6H_4CH_2CHO$, 104-09-6; 2-$MeC_6H_4CHCH_2O$, 2783-26-8; 2-MeC_6H_4CHO, 529-20-4; 2-$MeC_6H_4CH_2CHO$, 10166-08-2; 2,6-$Me_2C_6H_4CHCH_2O$, 78924-72-8; 2,6-$Me_2C_6H_4CHO$, 1123-56-4; 4-$MeOC_6H_4CHO$, 123-11-5; 4-$MeOC_6H_4CH_2CHO$, 5703-26-4; PhC-$(CH_3)CH_2O$, 2085-88-3; PhCOMe, 98-86-2; $PhCH(CH_3)CHO$, 93-53-8; O_2, 7782-44-7; norbornene, 498-66-8; styrene, 100-42-5; (*Z*)-β-methylstyrene, 766-90-5; (*E*)-β-methylstyrene, 873-66-5; (*Z*)-stilbene, 645-49-8; (*E*)-stilbene, 103-30-0; norbornene oxide, 278-74-0; 2-phenyloxirane, 96-09-3; *cis*-2-methyl-3-phenyloxirane, 4541-87-1; *trans*-2-methyl-3-phenyloxirane, 23355-97-7; (*Z*)-stilbene oxide, 1689-71-0; (*E*)-stilbene oxide, 1439-07-2; cyclooctene, 931-88-4; cyclohexene, 110-83-8; (*Z*)-2-hexene, 7688-21-3; (*E*)-2-hexene, 4050-45-7; octene, 25377-83-7; 9-oxabicyclo[6.1.0]nonane, 286-62-4; 7-oxabicyclo[4.1.0]heptane, 286-20-4; *cis*-2-methyl-3-propyloxirane, 6124-90-9; *trans*-2-methyl-3-propyloxirane, 6124-91-0; 2-hexyloxirane, 2984-50-1; *N*-pyridine oxide, 694-59-7; 4-picoline *N*-oxide, 1003-67-4; *para*-nitrostyrene, 100-13-0; *para*-nitrostyrene oxide, 6388-74-5; *para*-nitrobenzaldehyde, 555-16-8; benzylmethylketone, 103-79-7; chromous triflate, 55660-43-0; 8,8,8′,8′-tetramethylsalenH_2, 60306-02-7; triethylphosphine oxide, 597-50-2; bis(triethylphosphine oxide)(8,8,8′,8′)-tetramethylsalen)chromium(III)(trifluoromethone)sulfonate, 98759-96-7.