The final full-matrix least-squares refinement, minimizing the function $\sum w(|F_o| - |F_c|)^2$, converged to $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.034$ and $R_w = [\sum w(|F_o| - |F_c|)^2/(\sum w|F_o|^2)]^{1/2} = 0.036$ with unit weights. The error in an observation of unit weight was $S = [\sum w(|F_o| - |F_c|)^2/(n - m)]^{1/2} = 2.7$ with $n = 4751$ observations and $m = 261$ variables. An analysis of variance showed no unusual trends. In the last cycle of refinement the shifts for all parameters were less than 0.01σ, except for toluene parameters. A final difference Fourier map showed no excursion of electron density greater than 0.4 e/Å^3.

All calculations were performed on a VAX-11/730 DEC computer. The final fractional atomic coordinates are listed in Table IV. An ORTEP plot[34] of the molecule is shown in Figure 3.

Supplementary material is available from ref 7.

(c) Collection and Reduction of X-ray Data for RuHCl(dppm)$_2$·0.5PhMe. A preliminary photographic study with the help of a Weissenberg camera revealed that the crystals of RuHCl(dppm)$_2$·0.5PhMe belong to the monoclinic system and show systematic extinctions (0*k*0, $k = 2n + 1$; *h*0*l*, $l = 2n + 1$) consistent with the space group $P2_1/c$. The setting angles of 25 *hkl* reflections, regularly distributed in the half-sphere, automatically centered on an Enraf-Nonius CAD-4 diffractometer, were used in a least-squares calculation which led to the cell constants reported in Table V.

Table V also gives pertinent details concerning the experimental data collection conditions. Reflections have been recorded in three shells with the same crystal. Examination of the control reflection intensities, periodically measured, did not show a trend to decrease. Absorption corrections did not reveal to be necessary and were not performed.

(d) Structure Solution of RuHCl(dppm)$_2$·0.5PhMe. The structure has been solved by standard Patterson and Fourier syntheses. Conditions for refinement and used agreement indices R and R_w are defined as for 7. Values of the atomic scattering factors and the anomalous terms used for Ru, Cl, P, and C were from usual sources.[33,34] Scattering factors for hydrogen atoms were taken from Stewart et al.[35]

All calculations were performed using the SHELX-76 program[31] on a DPS8/Multics Honeywell-Bull-CII computer except for the last refinements which were performed on a VAX-11/730 DEC computer.

Because of the abundance of weak reflections (3954 with $F_o^2 > \sigma(F_o^2)$), we decided to consider the phenyl groups of the molecule as rigid groups. The Ru atom was located from the Patterson function. The positions of the remaining non-hydrogen atoms were obtained through the usual combination of full-matrix least-squares refinement and difference Fourier syntheses. The hydrogen atoms of the rigid groups were introduced in calculated positions. Those attached to the methylene carbon atoms as well as that linked to the ruthenium atom were found in the Fourier maps and refined, but they were assigned a fix isotropic thermal parameter U_{iso}. Furthermore, the methylenic H atoms were constrained to remain at a "distance" of 0.95 Å from the carbon atoms.

The presence in the crystal of disordered toluene molecules (crystallization solvent) created a particular problem. The molecule is located around the center of symmetry $^1/_2$, $^1/_2$, $^1/_2$ in such a way that (i) there are two symmetry-related principal locations of the phenyl ring, and (ii) two carbon atoms of one ring almost coalesce with two carbon atoms of the other ring. We were not successful in the location of the methyl group probably because of the existence of several orientations for this group. It was then decided to introduce in the refinement process only a rigid hexagonal group.

The last cycle of refinement led to the values $R = 0.046$ and $R_w = 0.045$ for the weighting scheme $w = 1.966/\sigma^2(F)$. A final difference Fourier map showed no excursion of electron density greater than 1 e/Å^3.

The final position and thermal parameters (U_{equiv} or U_{iso}) of all atoms but the hydrogen atoms of the phenyl groups are listed in Table VI.

Supplementary Material Available: Anisotropic thermal parameters and calculated hydrogen atom coordinates of the rigid phenyl groups as well as a listing of *h,k,l* and F_o and F_c (17 pages). Ordering information is given on any current masthead page.

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[36] Johnson, C. K. ORTEP; Oak Ridge National Laboratory: Oak Ridge, TN, 1965; Report ORNL-3794.

Selective Epoxidation of Olefins by Oxo[*N*-(2-oxidophenyl)salicylidenaminato]vanadium(V) Alkylperoxides. On the Mechanism of the Halcon Epoxidation Process

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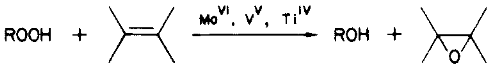
Abstract: Novel vanadium(V) alkylperoxy complexes with the general formula VO(OOR)(R′–OPhsal–R″) (II) [R = *t*-Bu, CMe$_2$Ph; R′–OPhsal–R″: Schiff base *N*-(2-oxidophenyl)salicylidenaminato tridendate ligand] were synthesized and characterized by physicochemical methods. These complexes most probably have a pentagonal pyramidal structure, with an axial vanadyl group and, in the pentagonal plane, three positions occupied by the Schiff base planar ligand and two positions occupied by a bidentate alkylperoxy group which is presumably weakly coordinatively bonded to the metal by the alkoxy oxygen atom. These complexes are very effective reagents for the selective transformation of olefins into epoxides, with yields ranging from 40% for 1-octene to 98% for tetramethylethylene. The reactivity of olefins is sensitive to steric hindrance and increases with the olefin nucleophilicity. The epoxidation of olefins by complexes II is stereoselective, inhibited by water, alcohols, and basic ligands or solvents, and accelerated in polar nondonor solvents. Kinetic studies showed that the olefin coordinates to the metal prior to the decomposition of the metal–olefin complex in the rate-determining step. Competitive epoxidation of several olefins vs. cyclohexene showed that the more strongly coordinated olefins exert an inhibiting effect on the epoxidation of the less strongly coordinated ones. These data, which are similar to those of the Halcon catalytic epoxidation process, are consistent with a pseudocyclic peroxy metalation mechanism.

Selective epoxidation of olefins by alkyl hydroperoxides catalyzed by d^0 metal complexes (Mo^{VI}, V^V, and Ti^{IV}) has become the most important industrial process for the manufacture of propylene oxide, due to the recent utilization of the *tert*-butyl alcohol coproduct as an octane booster in gasoline (Halcon process, eq 1, olefin = propylene, R = *t*-Bu, M = Mo).[1]



(1)

Despite intensive studies,[2] the mechanism of this reaction still remains a matter of controversy, since the nature of the actual

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[1] (a) Landau, R.; Sullivan, G. A.; Brown, D. *Chemtech* **1979**, 602. (b) Kollar, J. *Prepr.—Am. Chem. Soc., Div. Pet. Chem.* **1978**, *23*, 106.

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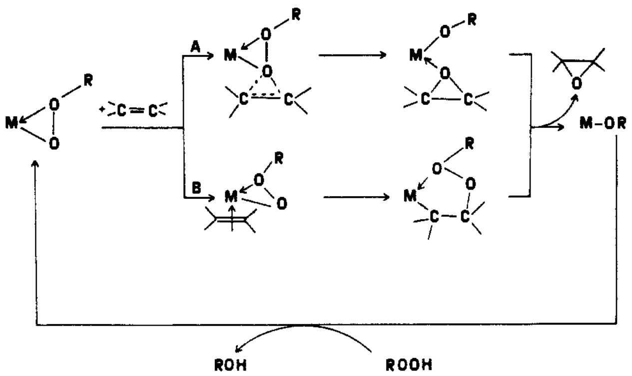
Table I. Vanadium(V) Alkylperoxy Complexes

				IR absorptions, cm$^{-1\,a}$			^{1}H NMR (t-Bu)^b		^{13}C NMR (t-Bu)^e				
complex	R	R′	R″	ν(V=O)	ν(O—O)	ν(V—O)	δ^c	$\Delta\delta^d$	$\delta(C_{Me_3})^c$	$\Delta\delta^d$	$\delta(CH_3)^c$	$\Delta\delta^d$	$M_w{}^f$
IIa	*t*-Bu	H	H	985	925	550	1.45	0.2	91.7	11.7	29.9	4.6	368
IIb	*t*-Bu	CH_3	H	990	915	565	1.45	0.2	91.4	11.4	29.9	4.6	382
IIc	*t*-Bu	Cl	H	985	908	557	1.48	0.23	92.7	12.7	30	4.7	402
IId	*t*-Bu	NO_2	H	990	890	590	1.5	0.25	93.1	13.1	30.3	5	410
IIe	*t*-Bu	Cl	Cl	999	925	560	1.48	0.23	92.9	12.9	30	4.7	437
IIf	CMe_2Ph	H	H	985	925	550	*g*	*g*		*g*			

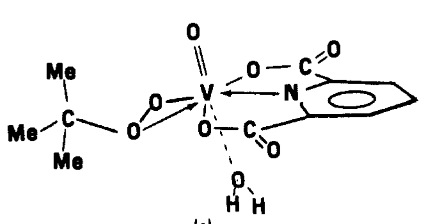
[a] KBr disk. [b] Solvent = CD_2Cl_2. [c] Reference = $SiMe_4$. [d] NMR shift vs. free *t*-BuOOH. [e] Solvent = $CDCl_3$. [f] Cryoscopic determination in benzene solution. [g] This complex is unstable in solution.

Scheme I



epoxidizing species has not been clearly established. However, in view of its very high selectivity and stereospecificity, it is generally accepted that it proceeds via a heterolytic rather than a homolytic mechanism. Two alternative mechanisms, A and B (Scheme I), which involve d^0 metal alkylperoxidic intermediates emerge from the numerous interpretations proposed:[3] (a) nucleophilic attack of olefin on the electrophilic oxygen atom covalently bonded to the metal, which is reminiscent of Bartlett's butterfly mechanism for epoxidation of olefins by percarboxylic acids;[2e,4,5] (b) coordination of the olefin to a metal followed by its insertion between the metal–oxygen bond, forming a five-membered pseudocyclic dioxametallocyclopentane, which decomposes by a 1,3-dipolar cycloreversion mechanism to the epoxide and the metal alkoxide, a process referred to as pseudocyclic peroxy metalation.[3,6]

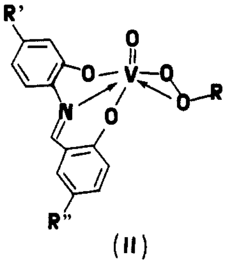
We have recently isolated and characterized by an X-ray crystal structure stable (dipicolinato)vanadium(V) alkylperoxidic complexes such as I,[7] in which the *tert*-butoxy oxygen atom of the OO-*t*-Bu group is sp^3-hybridized by coordination to vanadium, forming a triangular arrangement similar to that of peroxo complexes.[8]



(I)

However, complex I did not epoxidize olefins in a heterolytic way. This lack of activity was attributed to the lack of vacant or dissociable coordination site coplanar and adjacent to the alkylperoxidic moiety, for the coordination of the olefins.[7]

Therefore, synthesis of alternative stable vanadium(V) alkylperoxidic complexes that would epoxidize olefins has been undertaken. We were pleased to find that vanadium(V) alkylperoxidic complexes containing tridendate *N*-(2-oxidophenyl)salicylidenaminato Schiff base ligand (R′–OPhsal–R″) epoxidize olefins with high yields and selectivity. This paper reports on the synthesis and reactivity of such complexes (II).



(II)

Results

1. Synthesis and Characterization of VO(OOR)(R′–OPhsal–R″) Complexes. Addition of excess alkyl hydroperoxide to a $C_2H_4Cl_2$ solution of vanadyl isopropylate and the tridendate Schiff base *N*-(2-hydroxyphenyl)salicylidenamine or its derivative at 0 °C results in the formation of a deep-brown solution. Removal of the solvent followed by addition of a large excess of pentane yields the alkylperoxidic complexes II in good-to-excellent yields. These compounds were characterized by elemental analysis, infrared and NMR spectroscopies, and iodometric titration and correspond to the formula VO(OOR)(R′–OPhsal–R″) (II). These complexes are soluble in most organic solvents, stable in the solid state, safe to handle, and can be stored for months in the refrigerator.

Infrared spectra of the *tert*-butylperoxy complexes (Table I) showed the characteristic OO-*t*-Bu vibrations at 2980–2990 (ν(C—H)), 1175 (ν(C—C)), and 890–925 cm^{-1} (ν(O—O)), together with the characteristic ν(V=O) and ν(V—O(O-*t*-Bu)) frequencies at 985–1000 and 550–590 cm^{-1}, respectively.

^{1}H NMR spectra of the complexes (Table I) exhibited a singlet at δ 1.45–1.5 (solvent = CD_2Cl_2, reference Me_4Si) attributable to the *tert*-butyl group of the peroxidic moiety. This corresponds to a downfield shift $\Delta\delta$ with respect to the free *t*-BuOOH of ca. 0.2–0.25 ppm, which is much lower than that observed for the triangular dipicolinato complex **1** ($\Delta\delta$ = 0.6 ppm)[7] but higher than that of linear Pd–OO-*t*-Bu ($\Delta\delta$ = 0.1 ppm)[9] and Co–OO-*t*-Bu ($\Delta\delta \simeq -0.7$ ppm)[10] complexes. Besides, the ^{1}H NMR spectra of complexes IIa–e showed a singlet at δ 1.25 characteristic of free *t*-BuOH and representing ca. 15–20% of the total *t*-Bu groups. This indicates a partial decomposition of complexes (II) in solution. ^{13}C NMR spectra of complexes IIa–e confirm the presence of ca. 15% of free *t*-BuOH (δ(C–Me_3) 69.2, $\delta(CH_3)$ 30.6) and ca. 85% of coordinated OO-*t*-Bu groups ($\Delta\delta$(C–Me_3) = 11.4–13.1, $\Delta\delta(CH_3)$ = 4.6–5 ppm). The downfield ^{1}H and ^{13}C NMR shifts of the bonded OO-*t*-Bu groups increase with the electrophilic

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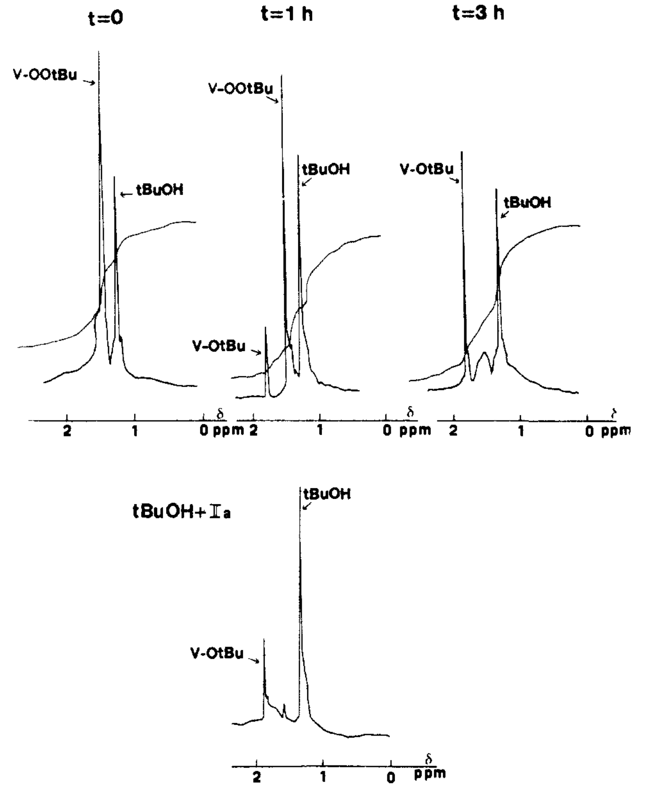


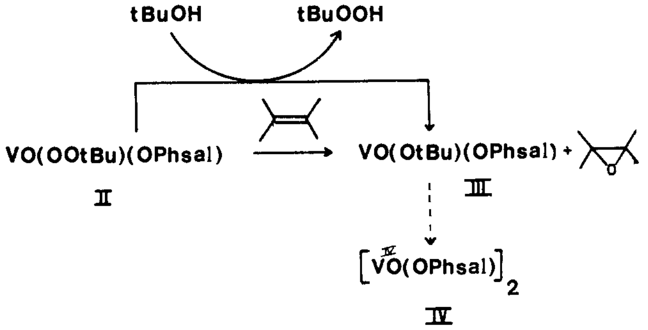
Figure 2. ^{1}H NMR monitoring in the *t*-Bu region of the epoxidation of styrene by IIa. Solvent, CD_2Cl_2. Reference $SiMe_4$.

nature of the substituents of the Schiff base in the order R′, R″ = NO_2, H > Cl, Cl > Cl, H > H, H > CH_3, H. Molecular weight measurements using cryoscopy in benzene indicated that the complexes IIa–e are monomeric in solution.

Despite extensive attempts, we have been unable to obtain suitable single cyrstals of complexes II for X-ray structure determination. However, on the basis of elemental analysis, IR, NMR, and molecular weight data, we suggest that complexes II have a pentagonal pyramidal structure. All the vanadium(V) peroxidic complexes isolated and X-ray characterized so far are seven-coordinated with a pentagonal bipyramidal geometry,[7,8,11] except for the compound $NH_4[VO(O_2)_2(NH_3)]$[12] which has a distorted pentagonal pyramidal structure similar to that of $CrO(O_2)_2$·py.[13] In these latter two pyramidal compounds, the metal is twice more displaced over the pentagon and toward the axial vanadyl oxygen atom as in pentagonal bipyramidal complexes. Since the vanadyl group V═O is always axial in peroxidic complexes, and since the tridendate R′—OPhsal—R″ ligand is planar,[14] it seems likely that the OOR group is bidentate as in complex I and occupies the two equatorial positions left in the pentagon. The lower downfield shift ($\Delta\delta$ = 0.2–0.25 ppm) of the O-*t*-Bu group observed by ^{1}H NMR of complexes IIa–e suggests that the O-*t*-Bu oxygen atom is much less coordinated to vanadium than in complex I and therefore that the V–O(*t*-Bu) distance is much longer than the V–O(O-*t*-Bu) distance. The lower affinity of the O(*t*-Bu) atom for vanadium in complexes II in comparison to complexes I is probably an important clue for interpreting their different reactivity.

2. Epoxidation of Olefins by Vanadium(V) Alkylperoxidic Complexes (II). 2.1. General Considerations. The stoichiometric oxidation of olefins by complexes IIa–e was carried out in N_2 at room temperature and in anhydrous solvents. A 10- to 50-fold excess of olefin with respect to the complex was used. The reaction was monitored by quantitative GC determination of the oxygenated products formed, and these products were identified by GC/MS coupling. No suitable method (iodometric, cerimetric, or UV titrations) was found to follow the consumption of active oxygen during the reaction. Figure 1 shows a typical epoxide formation vs. time when cyclohexene is oxidized by complex (IIa) at 30 °C in $C_2H_4Cl_2$ solution. No allylic oxidation products such as 2-cyclohexen-1-ol or 2-cyclohexen-1-one were formed during the reaction, with epoxycyclohexane being the only product (ca. 80% yield based on IIa) obtained.

Scheme II



A better approach to the features of this stoichiometric oxidation was revealed by using ^{1}H NMR monitoring during the reaction, as shown in Figure 2. The NMR spectrum of IIa in CD_2Cl_2 exhibited a singlet at 1.45 ppm (V–OO-*t*-Bu) and an other singlet at 1.25 ppm (15% of free *t*-BuOH resulting from the decomposition of IIa). Addition of excess styrene resulted in a continuous decrease of the singlet at 1.45 ppm and an appearance of a new signal at 1.85 ppm, while the singlet corresponding to *t*-BuOH remained approximatively constant. This new signal at 1.85 ppm was attributed to the reduced *tert*-butoxy complex VO(O-*t*-Bu)(OPhsal) (III). Attempts to isolate this complex in the solid state failed. Addition of excess pentane at the end of the reaction resulted in the precipitation of a vanadium(IV) dimeric complex identified as $[VO(OPhsal)]_2$ (IVa) and is similar to that obtained by Ginsberg from the reaction of $VOCl_2$ with HOPhsalH.[15] This dimeric vanadium(IV) complex probably results from the decomposition of the vanadium(V) alkoxo complex III. The *tert*-butoxy complex VO(O-*t*-Bu)(OPhsal) (III) has the same ^{1}H NMR shift of the O-*t*-Bu group (δ 1.85) as the known VO(O-*t*-Bu)(dipic)(H_2O).[7] Complex III can be generated in solution by addition of excess *t*-BuOH to the complex IIa, resulting in an anion exchange of the OO-*t*-Bu group by *t*-BuOH (Figure 2 and Scheme II). Scheme II sums up these different reactions, i.e., the epoxidation of olefins by IIa to give the *tert*-butoxy complex IIIa, the generation of IIIa from IIa with *t*-BuOOH, and the decomposition of IIIa to the V(IV) dimeric complex IVa.

Table II shows that for all but one olefin, epoxide was the only product detected, with the yield based on complex IIa ranging from 40% for 1-octene to 98% for tetramethylethylene (30 °C, 3 h, $C_2H_4Cl_2$). The epoxide yield as well as the reaction rate increases with the nucleophilic character of the olefin (vide infra). In analogy to molybdenum(VI) peroxo complexes,[16] but in contrast to the (dipicolinato)vanadium alkylperoxides I,[7] the epoxidation of olefins is completely stereoselective: *cis*-2-butene was transformed only to *cis*-2,3-epoxybutane (entry 11) and *trans*-2-butene exclusively to *trans*-2,3-epoxybutane (entry 12). Norbornene only gave *exo*-epoxynorbornane. Styrene gave a mixture of epoxide and benzaldehyde. The aldehyde is formed in a consecutive oxidative cleavage of the epoxide by IIa. Allylic alcohol was found

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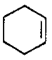
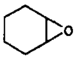
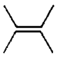
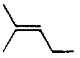
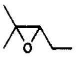
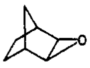
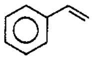
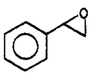
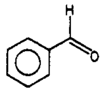
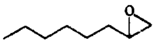
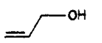
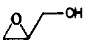
Table II. Epoxidation of Olefins by Vanadium(V) Alkylperoxidic Complexes (II)[a]

entry	complex	substrate	product(s),[b] yield, %[c]	
				
1	IIa		80	
2	IIb		82	
3	IId		75	
4	IIe		78	
5	IIa + H_2O[d]		26	
6	IIa + *t*-BuOH[d]		13	
				
7	IIa		98	
				
8	IIa		93	
				
9	IIa		82	
10	IIa + HMPT[f]		6	
				
11	IIa		70	
				
12	IIa		65	
				
13	IIa		48	20
				
14	IIa		40	
				
15	IIa		0	

[a] Reaction conditions = temperature, 30 °C; solvent, $C_2H_4Cl_2$; complex = 0.03 M; olefin = 1.5 M; time = 180 min. [b] Identified by GS/MS coupling. [c] GC determination using various internal standards—yields are based on vanadium. [d] Addition of 5 equiv of H_2O or *t*-BuOH at the beginning of the reaction. [e] Addition of 1 equiv of HMPT.

to be nonreactive, in contrast to the catalytic epoxidation of olefins by alkyl hydroperoxides in the presence of vanadium compounds.[2,17] This can be readily explained by displacement of the OO-*t*-Bu group in the complex by excess allylic alcohol.

Addition of strongly donor ligands such as HMPT almost completely inhibits the epoxidation (entry 10), presumably by preventing the coordination of the olefin to the metal. The reaction was also strongly retarded by addition of small amounts of water (entry 5), which hydrolyzed the V–OO-*t*-Bu bond, and inhibited by the presence of *t*-BuOH (entry 6), which displaced the alkyl hydroperoxide from the metal. The same characteristics were found in other catalytic epoxidation of olefins by alkylhydroperoxides.[2e]

The substituents of the Schiff base ligand OPhsal have no major effect on the rate and the selectivity of the epoxidation of cyclohexene by complexes IIa–e. Only a small increase in the yield resulted from increasing the nucleophilicity of the substituents (entries 1–4).

2.2. Kinetic Studies. Reaction rates of olefin epoxidation by complex IIa were determined by monitoring the formation of epoxide vs. time by GC. Figure 3 shows that the initial rate (until ca. 50% conversion of IIa) of the stoichiometric epoxidation of cyclohexene by IIa linearly increases with the concentration of the oxidant, while the plot of initial velocity vs. cyclohexene concentration has a hyperbolic form (Figure 4). This kinetic scheme is similar to that of the epoxidation of olefins by molybdenum peroxo complexes[16] and is described by the Michaelis–Menten equation, frequently encountered in enzymatic reactions[18,19] (eq 2 with L = OPhsal, $K = k_1/k_{-1}$, and rds = rate-determining step).

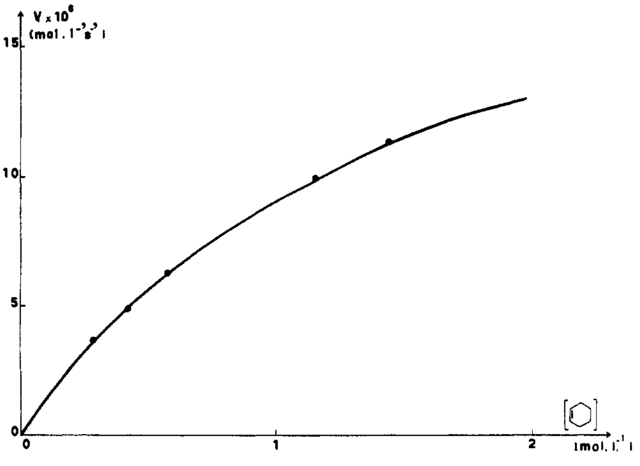


Figure 4. Variation of the initial rate of epoxidation of cyclohexene by IIa vs. cyclohexene concentration. Temperature, 30 °C; solvent, $C_2H_4Cl_2$; complex, 0.03 M.

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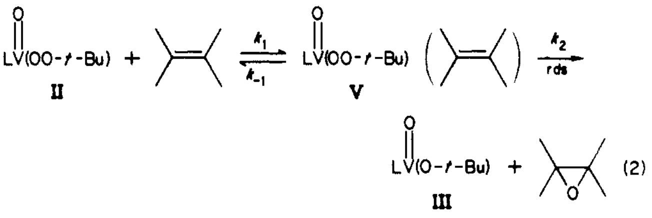
[18] Michaelis, L.; Menten, M. L. *Biochem. Z.* **1913**, *49*, 333.

[19] Collman, J. P.; Brauman, J. L.; Meunier, B.; Haysishi, T.; Kodadek, T.; Raybuck, S. A. *J. Am. Chem. Soc.* **1985**, *107*, 2000.



(2)

The complex II and olefin reversibly interact to form a metal–olefin complex V which irreversibly decomposes in the rate-determining step to produce the epoxide and the *tert*-butoxy complex III.

Such a kinetic scheme is described by eq 3, where K is a measure of the bonding affinity of the olefin to the metal, k_2 is the rate-determining step constant of the decomposition of the metal–olefin complex, and k' is the specific rate at [olefin] = 1 mol·L^{-1}.

$$V = -\frac{d[\mathrm{II}]}{dt} = \frac{d[\mathrm{epoxide}]}{dt} = \frac{k_2K[\mathrm{II}][\mathrm{olefin}]}{1 + K[\mathrm{olefin}]} = k'[\mathrm{II}] \quad (3)$$

The values of k_2 and K were respectively calculated from the intercept and the slope of the straight line obtained by plotting the reciprocal of initial velocity vs. the reciprocal of olefin concentration, for a given initial concentration of complex (II) (eq 4).

$$\frac{1}{V} = \frac{1}{k_2[\mathrm{II}]} + \frac{1}{Kk_2[\mathrm{II}][\mathrm{olefin}]} \quad (4)$$

Figure 5 shows that straight lines were indeed obtained from the individual oxidation of several olefins, allowing k_2 and K_i to be determined (K_i = individual coordination constant of the olefin to the metal), which are reported in Table III.

In general, the specific rate k' increases with k_2 and K_i; further, there is a parallelism between k_2 and K_i. The reactivity of olefins increases with their coordination constant associated with their nucleophilic character, following the order tetrasubstituted > trisubstituted > disubstituted > monosubstituted, as shown previously for the epoxidation of olefins by molybdenum peroxo complexes.[16] However, the difference in reactivity between trisubstituted olefins and disubstituted olefins is somewhat lower than in the previous case. The lower reactivity of 2,4,4-trimethyl-2-pentene compared to that of 2-methyl-2-pentene, as illustrated by a lower value of k_2 and K_i, is attributed to great steric hindrance in both the olefin coordination and in the decomposition of the intermediate V.

The reactivity ratio of norbornene to cyclohexene, equal to 2.24, is close to the value of 1.94 obtained by Sharpless for epoxidation by MoO_5·HMPT complex.[20] Norbornene has a lower coordination constant k_i but a much higher rate constant k_2 than cyclohexene, presumably due to the strain energy loss of the double bond in the rate-determining step (vide infra).[21]

Further evidence in favor of the olefin coordination step was provided by the competitive epoxidation of two different olefins by the vanadium(V) *tert*-butylperoxidic complex IIa. For two olefins A and B, the relative rate values can be obtained by using eq 5 where dE_A/dt and dE_B/dt represent the initial velocity of

$$\frac{-d(A)/dt}{-d(B)/dt} = \frac{dE_A/dt}{dE_B/dt} = \frac{[A]}{[B]}\frac{k_2^AK_C^A}{k_2^BK_C^B} \quad (5)$$

epoxide formation E_A and E_B from olefins [A] and [B], [A]/[B] represents the ratio of initial concentrations of A and B, k_2^A and k_2^B represent the rate constants of A and B, and K_C^A and K_C^B represent the coordination constant of A and B under competitive conditions.[19,22] Plots of the ratio of initial rates $(-dE_A/dt)/(-dE_B/dt)$ vs. the ratio of initial concentrations of olefins gave straight lines, as shown in Figure 6. The slope $k_2^AK_C^A/k_2^BK_C^B$ of these straight lines gives the value of the competitive coordination constant K_C^A (Table III) with respect to that of cyclohexene K_C^B taken as reference (k_2^A and k_2^B are known from the individual experiments and are given in Table III).

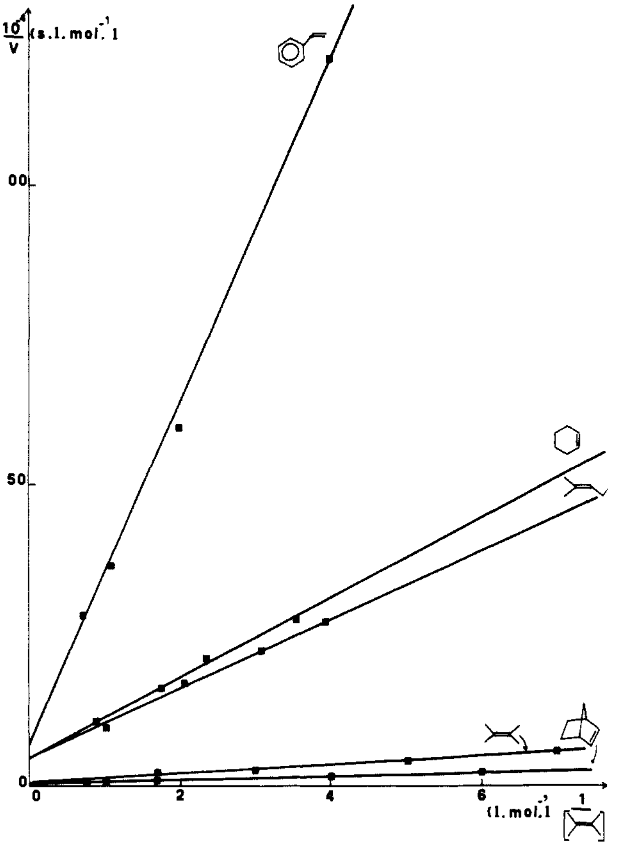


Figure 5. Variation of the reciprocal of initial rate of the epoxidation of various olefins by IIa vs. the reciprocal of olefin concentration. Temperature, 30 °C; solvent, $C_2H_4Cl_2$; IIa, 0.03 M.

Table III shows that K_C is higher than K_i for the olefins which coordinate more than cyclohexene (tetramethylethylene, 2-methyl-2-pentene), whereas K_C is lower than K_i for the olefins that coordinate less than cyclohexene (norbornene, styrene). This means that the more coordinating olefin exerts an inhibitory effect on the coordination and therefore the reactivity of the other competing olefin. This is strikingly illustrated in the case of norbornene vs. cyclohexene competition: Norbornene reacts faster than cyclohexene in individual experiments since its k_2 is higher, but the reverse occurs under competitive conditions since its K_i is lower (see Figure 7).

Table IV reports the solvent effect observed during the epoxidation of cyclohexene by IIa. The best solvents were found to be $C_2H_4Cl_2$ and Ph–NO_2, characterized by low donicity (D_N) and the high dielectric constant (ϵ). The reaction proceeds at a lower rate in nonpolar solvents such as benzene or toluene. Basic solvents such as THF and DMF characterized by high donicity completely inhibit the reaction. This solvent effect, characterized by an increase in velocity with the dielectric constant of nonpolar solvents, is similar to that previously observed for stoichiometric epoxidation by MoO_5·HMPT[16] and the Mo-catalyzed epoxidation of olefins by ROOH.[2b]

The activation energy of the epoxidation of cyclohexene by IIa ($C_2H_4Cl_2$, temp = 10–30 °C), E_A = 12.5 ± 0.5 kcal·mol^{-1}, is in the same range as that obtained (11.5 kcal·mol^{-1}) from the catalytic epoxidation of cyclohexene by t-BuOOH in the presence

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(21) Schmid, G. H.; Garrat, D. G. *The Chemistry of the Double-Bonded Functional Groups*; Patai, S., Ed.; Wiley: New York, 1985; Part II, pp 725–912.

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(23) Reichardt, C. *Solvent Effects in Organic Chemistry*; Verlag: Weinheim, New York, 1979; pp 17 and 270.

Table III. Kinetic Data from the Epoxidation of Various Olefins by Complex IIa in Individual and Competitive Experiments[a]

olefin	specific rate $10^5k'$ at [olefin] = 1 mol·L^{-1}, s^{-1}	rate const 10^3k_2, s^{-1}	individual coord const K_i, L/mol	competitive coord const K_c, L/mol
tetramethylethylene	170	2.47	2.2	2.77
2-methyl-2-pentene	41.5	1.01	0.7	1.02
2-methyl-2-butene	62.8	1.41	0.8	nd
2,4,4-trimethyl-2-pentene	16.7	0.45	0.59	nd[b]
cyclohexene	31.1	0.91	0.52	0.52 (ref)
norbornene	69.6	2.21	0.46	0.32
styrene	9.1	0.35	0.35	0.15

[a] Reaction conditions = temperature 30 °C; solvent, $C_2H_4Cl_2$; complex IIa = 0.03 M. [b] Not determined.

Table IV. Solvent Effect for Epoxidation of Cyclohexene by IIa[a]

solvent	$\epsilon_{25°C}$[b]	D_N[c]	rate 10^5V, mol·L^{-1}·s^{-1}	% yield[d]
$C_2H_4Cl_2$	10.1	0	1.33	80
Ph-NO_2	35.9	4.4	1.21	90
Ph-Cl	5.6		1.05	70
Ph-CH_3	2.4		0.9	65
C_6H_6	2.3	0.1	0.4	60
CH_3CN	38	14.1	0.4	67
THF	7.6	20	e	0
DMF	36.7	26.6	e	0

[a] Reaction conditions = temperature, 30 °C; IIa, 0.03 M; cyclohexene; 1.5 M. [b] Dielectric constants at 25 °C taken from ref 23. [c] Solvent donor number vs. $SbCl_5$ taken from ref 23. [d] GC determination; yields are based on IIa. [e] Nonmeasurable reaction rate.

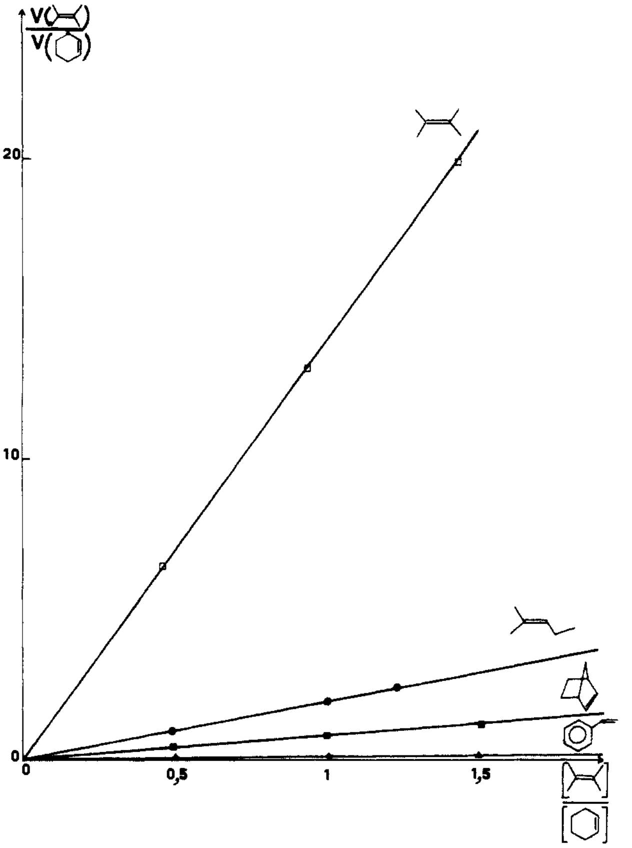


Figure 6. Variation of the ratio of the initial velocities of epoxidation of cyclohexene and a competing olefin vs. the ratio of olefin concentrations. Temperature, 30 °C; solvent, $C_2H_4Cl_2$; IIa, 0.03 M.

of $VO(acac)_2$[24] but lower than that of epoxidation by MoO_5·HMPT (E_A = 15.9 kcal·mol^{-1}).[16]

2.3. Catalytic Epoxidation of Cyclohexene by *tert*-Butyl Hydroperoxide. Vanadium compounds are known to be much less efficient catalysts than molybdenum compounds for the epoxidation of nonactivated olefins by t-BuOOH.[24] Table V shows that the nature of the ligand exerts a dramatic influence on both the yields and selectivity of the epoxidation of cyclohexene by *t*-BuOOH. Whereas VO(O-*i*-pr)$_3$ and complex IIa catalyze the formation of epoxycyclohexane as the main product, complex I and VO(salen) mainly give allylic oxidation products in low yields, together with slight formation of epoxide. These results are consistent with the oxidizing properties of complexes I and II previously observed under stoichiometric conditions. Complex I is an essentially homolytic reagent which hydroxylates alkanes, olefins, and arenes,[7] whereas complex II is an essentially heterolytic reagent which only epoxidizes olefins.

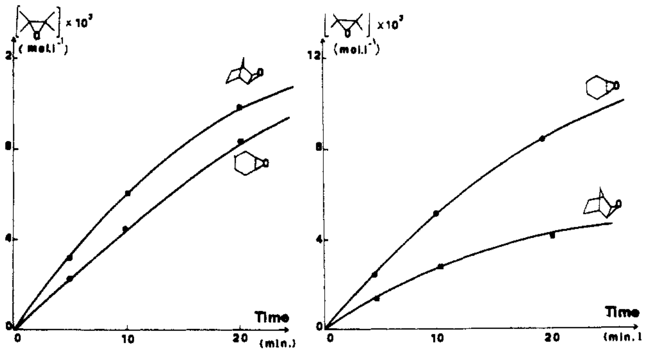
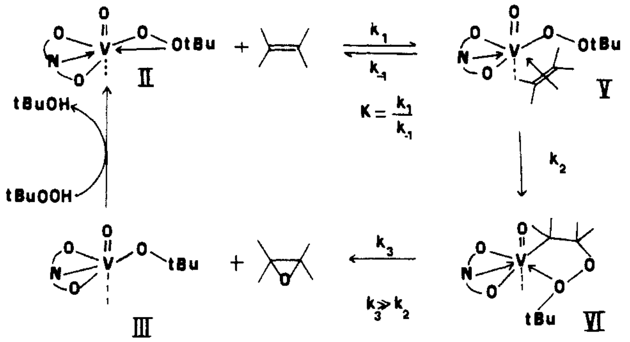


Figure 7. Stoichiometric epoxidation of cyclohexene and norbornene by IIa (a, left) in individual experiments and (b, right) in competitive experiments. Solvent, $C_2H_4Cl_2$; olefin/cyclohexene = 1:1; IIa, 0.03 M.

Scheme III



Discussion

V^{V}O(OOR)(R–OPhsal–R″) complexes (II) are the first well-defined examples of d^0 metal alkylperoxidic species which epoxidize olefins with high selectivity. Their reactivity is highly relevant to the d^0 metal-catalyzed epoxidation of olefins by alkyl hydroperoxides. It is also close, but not similar, to the reactivity of the molybdenum(VI) peroxo complex MoO_5·HMPT. However, it strongly differs from that of the V^{V}O(OOR)(dipic)L complex. The epoxidation of olefins by complexes II has the following characteristics:

(i) The reaction is highly stereoselective: *cis*-olefins yield *cis*-epoxides, and *trans*-olefins yield *trans*-epoxides. The reactivity of olefins increases with their nucleophilic character and is largely influenced by steric effects.

(ii) The reaction is strongly inhibited by water, alcohols, and basic solvents and is accelerated in nondonor polar solvents.

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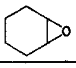
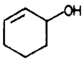
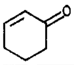
[24] Su, C. C.; Reed, J. W.; Gould, E. S. *Inorg. Chem.* **1973**, *12*, 337.

Table V. Catalytic Epoxidation of Cyclohexene by *t*-BuOOH[a]

complex	*t*-BuOOH[b] conversion, %	products, % yields[c]		
				
VO(O-*i*-pr)$_3$	80	62.5	0.7	0.7
VO(OO-*t*-Bu)(OPhsal) (II)	75	43	1	1
VO(OO-*t*-Bu)(dipic)(HMPT) (I)	89	0.9	2.6	3.3
VO(salen)[d]	88	0.1	4.4	5.8

[a] Reaction conditions: temp, 60 °C; solvent, $C_2H_4Cl_2$; *t*-BuOOH, 1.43 M; cyclohexene, 1.40 M; complex, 0.07 M, reaction time, 3 h. [b] *t*-BuOOH concentration measured by iodometric titration. [c] GC yields based on *t*-BuOOH consumed. [d] Salen = *N*,*N'*-bis(salicylaldehyde)ethylenediamine.

(iii) Kinetic studies show that the olefin coordinates to the metal prior to the decomposition of the metal–olefin complex in the rate-determining step. Competitive epoxidation of several olefins illustrates the predominance of the olefin coordination over the other characteristics of the reaction.

The mechanism of the epoxidation of olefins by complexes II depicted in Scheme III provides a plausible interpretation of our experimental results:

(i) The olefin reversibly bonds to the metal to give the metal–olefin complex. Of the two available coordination sites, the axial one, trans to the vanadyl group, is too weak to activate olefins, as in other d^0 metal peroxo complexes.[6,8] The only possible position is therefore that occupied by the weakly coordinated O(*t*-Bu) atom which could be displaced by the olefin. The adjacent and coplanar situations of the olefin and the peroxidic group on the metal are probably similar to that previously deduced from the reactivity of Mo–peroxo complexes.[6c] The nature of the metal–olefin interaction is a pure Lewis acid–Lewis base bond since vanadium(V) has no d electrons available for back-bonding to the olefin. It is therefore expected that the more easily coordinated olefins will be those having increasing substitution by electron-donating groups. This is indeed observed, particularly in competitive experiments, where the more coordinated olefins (higher K_i values) inhibit the epoxidation of the competing olefin. The strong inhibition of the epoxidation by σ donor solvents and ligands can also be interpreted by competition with olefins to occupy the coordination site of vanadium.

(ii) This step is rate determining and consists of the migratory insertion of the olefin between the vanadium–oxygen bond (π–σ rearrangement), which results from the nucleophilic attack of the bonded oxygen atom on the coordinated electron-deficient olefin. The solvent effect observed indicates that the activated intermediate is polarized and suggests that nondonor polar solvents enhance the charge separation of the dipole in the rate-determining step.[23] It is indeed expected that the polarization of $V^{\delta+}$–$O^{\delta-}$(O-*t*-Bu) will favor the insertion of olefin between the V–O bond, which results in the formation of the pseudocyclic dioxametallocyclopentane (VI) closed by coordination of the δ oxygen atom (O-*t*-Bu) to the metal. This has already been shown to occur in the case of the ketonization of terminal olefins by Pd–OO-*t*-Bu complexes.[9] The high rate constant k_2 observed in the case of norbornene can be attributed to a loss of strain energy (ca. 10 Kcal·mol^{-1})[25] resulting from the opening of the double bond in the rate-determining step.

(iii) This step consists of the rapid decomposition ($k_3 \gg k_2$) of the pseudocyclic dioxametallocyclopentane by a 1,3 dipolar cycloreversion process, resulting in the formation of the epoxide and vanadium(V) *tert*-butoxy complex III. Bond-breaking during cycloreversion have been shown by theoretical studies to occur as a metal–carbon electron pair transfer to the O–O σ^* orbital.[26] A similar mechanism has been proposed for the epoxidation of olefins by Mo–peroxo complexes[16] and by Pd–NO_2 complexes.[27]

(iv) The catalytic epoxidation of olefins by alkyl hydroperoxides (Halcon process) results from the displacement of the alkoxy group in complex III by excess ROOH, resulting in the liberation of alcohol coproduct and the regeneration of the initial alkylperoxy complex II. The autoretardation effect by the alcoholic coproduct can be readily explained by the competition with the hydroperoxide by forming metal–alkoxy bonds.

The general characteristics of the Halcon epoxidation process are in agreement with the features of the stoichiometric epoxidation of olefins by complex II: same order of reactivity of olefins, same stereoselectivity, same Michaelis–Menten kinetics,[2,28] same solvent effects,[2b] same inhibition by H_2O, ROH, and σ donor ligands, and similar activation energy.[24] Complexes II can therefore be considered as good models for the Halcon epoxidation process.

Epoxidation of olefins by complexes II is similar to that by Mo–peroxo complexes, with some noticeable difference such as the inhibition by alcohols and the lower activation energy. In contrast to the epoxidation by d^0 metal peroxo complexes which requires two anionic positions for the peroxo group and one coordination position for the olefin, the epoxidation by complex II requires only one anionic position for the OOR group and one coordination position for the olefin. This could explain the catalytic properties of molybdenum[5a] and titanium[5b] porphyrin complexes in the Halcon epoxidation reaction.[30]

The nature of the ligand plays an essential role in the reactivity of vanadium(V) alkylperoxidic complexes. The heterolytic reactivity of the Schiff base complexes II is probably due to the fact that the O–(*t*-Bu) oxygen atom is weakly bonded to the metal, whereas in the dipicolinato complex I the strong bonding of the O–(*t*-Bu) oxygen atom prevents the coordination of the olefin and therefore the heterolytic reaction from occurring. Hence, the coordination of olefin to the metal, as in most heterolytic oxidation by peroxides,[6] is an essential prerequisite for selective oxidation processes.

Experimental Section

Apparatus. Infrared spectra were recorded by a Perkin-Elmer Model 1430, ^{1}H NMR spectra by a Varian CFT 20, and ^{13}C NMR spectra by a Brucker CXP 200 spectrometers. Products were identified by GC/MS coupling (KRATOS Model MS 80) and comparison with the mass spectra of authentic samples.

Materials. VO(O-*i*-Pr)$_3$, 80% *tert*-butyl hydroperoxide (Merck), and 80% cumyl hydroperoxide (Merck) were used as received for the synthesis of the alkylperoxy complexes. Schiff base ligands were prepared by condensing the *O*-aminophenol with the salicylic aldehyde in absolute ethanol according to a known procedure.[29]

Solvents ($C_2H_4Cl_2$, CH_3CN) were distilled over CaH_2 before use; olefins were passed through a column containing active alumina to remove peroxidic impurities, distilled over sodium, and stored in nitrogen.

The solution of *tert*-butyl hydroperoxide in $C_2H_4Cl_2$ used in catalytic experiments was obtained by careful vacuum distillation of the aqueous 70% commercial solution (Akzo) according to the procedure described by Sharpless.[2e]

Preparation of Oxo[*N*-(2-oxidophenyl)salicylidenaminato]vanadium(V) Alkylperoxides (II). The complexes were prepared by the same procedure. VO(O-*i*-Pr)$_3$ (4 mol) was reacted with 1 equiv of the Schiff base

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[28] Megdiche, R.; Schnurpfeil, D. *J. Prakt. Chem.* **1983**, *325*, 113.

[29] Westland, A. D.; Tarafder, M. T. H. *Inorg. Chem.* **1983**, *20*, 8992.

[30] Whereas molybdenum[5a] and titanium[5b] porphyrin peroxo complexes are stoichiometrically inactive, TiO(TPP) and MoO_2(TPP) are catalysts for the epoxidation of olefins by *t*-BuOOH. This has been used as an argument against the peroxy metalation mechanism. However, since two coordination positions exist over the porphyrin plane, the reaction between an end-bonded OO-*t*-Bu group and a vicinal coordinated olefin is not inconceivable, whereas this possibility does not exist for bidendate porphyrin peroxo complexes.

ligand in 20 mL of $C_2H_4Cl_2$ at room temperature. Addition of excess 80% ROOH to the solution at 0 °C resulted in a deep-brown solution which was concentrated at 20 °C in vacuo. Addition of excess pentane resulted in the precipitation of the expected complexes in a pure form. These complexes are stable in the solid state if kept in a refrigerator. They are soluble in most organic solvents except alkanes.

VO(OO-*t*-Bu)(OPhsal) (IIa). Yield 80%. Anal. Calcd for $VC_{17}H_{18}NO_5$: C, 55.59; H, 4.90; N, 3.81; O, 21.8; active oxygen, 4.36. Found: C, 55.38; H, 4.78; N, 3.86; O, 21.70; active oxygen (by iodometry), 4.38.

VO(OO-*t*-Bu)(CH_3OPhsal) (IIb). Yield 78%. Anal. Calcd for $VC_{18}H_{20}NO_5$: C, 56.69; H, 5.25; N, 3.67; O, 21.0; active oxygen, 4.2. Found: C, 56.43; H, 5.19; N, 3.80; O, 20.78; active oxygen, 4.3.

VO(OO-*t*-Bu)(ClOPhsal) (IIc). Yield 80%. Anal. Calcd for $VC_{17}H_{17}NO_5Cl$: C, 50.81; H, 4.23; N, 3.49; O, 19.92; Cl, 8.84; active oxygen, 3.99. Found: C, 50.56; H, 4.15; N, 3.56; O, 19.74; Cl, 8.67; active oxygen, 4.0.

VO(OO-*t*-Bu)(NO_2OPhsal) (IId). Yield 85%. Anal. Calcd for $VC_{17}H_{17}N_2O_7$: C, 4..51; H, 4.13; N, 6.8; O, 27.18; active oxygen, 3.88. Found: C, 49.2; H, 4.05; N, 6.62; O, 26.97; active oxygen, 3.9.

VO(OO-*t*-Bu)(ClOPhsalCl) (IIe). Yield 70%. Anal. Calcd for $VC_{17}H_{16}NO_5Cl_2$: C, 46.79; H, 3.67; N, 3.21; O, 17.32; Cl, 16.28; active oxygen, 3.67. Found: C, 43.3; H, 3.37; N, 3.58; O, 17.06; Cl, 16.05; active oxygen, 3.75.

VO(OOCMe_2Ph)(OPhsal) (IIf). Yield 68%. Anal. Calcd for $VC_{22}H_{20}NO_5$: C, 61.54; H, 4.66; N, 3.26; O, 18.64; active oxygen, 3.73. Found: C, 61.18; H, 4.54; N, 3.45; O, 18.31; active oxygen, 3.85.

Preparation of [VO(OPhsal)]$_2$ (IVa). Cyclohexene (5 mL) dissolved in 20 mL $C_2H_4Cl_2$ was added to a solution of 367 mg of IIa (1 mmol) in 10 mL of $C_2H_4Cl_2$ at 30 °C. The epoxidation took place for 3 h. At the end of the reaction, addition of excess pentane resulted in the precipitation of IVa. Yield 75%. Anal. Calcd for $V_2C_{26}H_{18}N_2O_6$: C, 56.1; H, 3.24; N, 5.03; O, 17.27. Found: C, 55.7; H, 3.21; N, 4.9; O, 17.1. The same complex was prepared from the reaction of $VOCl_2$ with 1 equiv of OPhsalH_2 in EtOH according to the method of Ginsberg.[15]

Oxidation Procedure and Product Analysis. The olefins were stoichiometrically oxidized by complexes II in a thermostated Schlenck apparatus connected to a vacuum N_2 line. In a typical experiment, the olefin (5 mmol) was added in N_2 to the solution of complex II (0.1 mmol) in $C_2H_4Cl_2$ (3 mL), and the mixture was stirred at the required temperature (30 °C). The reaction was followed by GC quantive analysis of aliquot samples quenched by addition of excess triphenylphosphine to destroy the remaining peroxide. Various internal standards were used: *o*-dichlorobenzene for cyclohexene, norbornene, styrene, and 1-octene (column = FFAP 10% on Chromosorb GCQ 3 m); *n*-propylacetate for 2-butenes, 2-methylpentene, tetramethylethylene (column = Carbowax 20M on Chromosorb WAWDMCS).

Kinetics. All the runs for liquid olefins were carried out under ambient pressure with dry N_2 in a 10-mL Schlenck glass flask. The reaction was started by addition of olefin to the dry $C_2H_4Cl_2$ solution of II. All reaction rates are determined at early reaction times (<50% conversion) and are reproducible to within 10%. When the initial concentration of olefin was changed, e.g., for the experiments described in Figures 4 and 5, the corresponding amount of paraffin was added to keep the total amount of hydrocarbon constant, thus avoiding a change in the solvent effect.

The catalytic epoxidation was carried out as follows. To a solution of vanadium complex (0.1 mmol) in $C_2H_4Cl_2$ (3 mL), 20 equiv of cyclohexene and 20 equiv of pure *t*-BuOOH dissolved in $C_2H_4Cl_2$ were added. The reaction was followed by GC analysis of aliquot sample and iodometric titration of the *t*-BuOOH consumed.

Supplementary Material Available: Epoxide formation vs. time in the oxidation of cyclohexene by IIa (Figure 1) and plot of the initial rate of epoxidation of cyclohexene by IIa vs. concentration (Figure 3) (2 pages). Ordering information is given on any current masthead page.

Carbenoid Anion Behavior of Dilithio Derivatives of Thioacetal Alcohols. Stereochemistry and Mechanism of Ring Closures by Oxyanion-Facilitated CH Bond Insertion

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Abstract: Like other lithio derivatives of thioacetals bearing a second anionic site, dilithio derivatives of 3,3-, 5,5-, and 6,6-bis(phenylthio) alcohols decompose at or below ambient temperature to yield products ascribable to carbenoid intermediates. The 5,5-derivatives decompose far faster than the other types, and they yield mainly 2-(phenylthio)cyclopentanols and none of the unsaturated alcohols and glycols, arising from 1,2-hydrogen transfer and carbenoid dimerization, respectively, which are the major products from the other two types of reactants. The five-membered ring formation observed in the 5,5-systems results from insertion of a carbenoid carbon atom into the activated carbinol CH bond of the oxyanion, and a stereochemical study reveals that this process is not concerted. The evidence suggests that this ring closure is a result of displacement of a thiophenoxide ion from the lithiothioacetal by a hydride ion which is transferred from the carbinyl carbon atom in a transition state involving coordination of the lithium atom of the carbenoid with the oxyanion.

Recently, we proposed the following principle which has led to the discovery of several new reaction types: Normally stable lithio salts of diphenyl thioacetals, when they are contained in molecules possessing another anionic site, decompose to products which can be ascribed to carbene-like species, and the behavior of the latter may be controlled by the nature and position of the other anionic site.[1] Among several examples[2–4] of this phenomenon which have been discovered in this laboratory are the conversion of the dilithio derivatives **1** and **3** to **2** and **4**, respectively. A particularly intriguing example is the conversion of **5** mainly to **8** and to only a small quantity of the six-membered analogue of **4**;[1] it was proposed that one of the thioacetal anionic groups decomposes to or behaves like a carbene (see **6**) which inserts into the weak[5] CH bond adjacent to the other negatively charged carbon atom to yield the intermediate lithiothioacetal **7**.

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