

On the Mechanism of Oxygen Atom or Nitrene Group Transfer in Reactions of Epoxides and Aziridines with Tungsten(II) Compounds

Lauren M. Atagi, Diana E. Over, Donald R. McAlister,¹ and James M. Mayer*²

Contribution from the Department of Chemistry, University of Washington, Seattle, Washington 98195. Received May 10, 1990

Abstract: The tungsten(II) complexes $WCl_2(PMePh_2)_4$ (**1**) and $WCl_2(CH_2=CH_2)_2(PMePh_2)_2$ (**2**) react with epoxides and aziridines to form tungsten(IV)-oxo and -imido complexes. The relative reactivities of epoxides with **2** have been determined from competition experiments. More substituted epoxides are harder to deoxygenate: the reactivities of ethylene, isobutylene, and tetramethylethylene oxides fall in the geometric progression 100:10:1. *cis*-2-Butene oxide is deoxygenated faster than its *trans* isomer. Reaction occurs with predominant ($\geq 85\%$) retention of configuration (e.g. *cis* epoxides to *cis* olefins). The reaction of **2** with ethylene-*d*₄ oxide yields $W(O)Cl_2(CH_2=CH_2)(PMePh_2)_2$ (**4**) and uncoordinated $CD_2=CD_2$. The data suggest that de-epoxidation occurs via oxygen atom abstraction, and not via an oxametallacyclobutane which rearranges to an oxo-ethylene complex. Similarly, the tungsten center is suggested to attack the nitrogen atom of the aziridines, rather than react by initial oxidative addition of a C-N bond. This is indicated by the observation of an N-bound complex of aziridine and by the much slower rates of reaction for aziridines with bulky substituents on the nitrogen. The reactivities of para-substituted styrene epoxides are not strongly affected by the nature of the substituent (a ρ^+ value of -0.5 is calculated with Hammett σ^+ parameters) indicating that the transition state is not very polar, although there appears to be some conjugation between the phenyl ring and the epoxide. In sum, the data are most consistent with either concerted oxygen or nitrene transfer to tungsten or a mechanism involving a short-lived radical intermediate.

The mechanism(s) of olefin epoxidation by metal-oxo compounds and the reverse reaction, the formation of metal-oxo complexes by deoxygenation of epoxides, have attracted a great deal of interest in recent years.³⁻¹⁴ Epoxides are valuable in-

termediates in synthetic organic chemistry, are prepared on an industrial scale,¹⁵ and are important enzymatic products.¹⁶ A wide variety of metal reagents have been used in the laboratory to effect epoxidation or de-epoxidation, from titanium to nickel species, from porphyrin to halide to cyclopentadienyl complexes, and from isolated compounds to materials generated in situ. Similarly, a number of mechanisms have been suggested for these reactions, including concerted, radical, carbocation, and organometallic pathways.

We recently reported the deoxygenation of ethylene oxide and propylene oxide by the tungsten(II) complex $WCl_2(PMePh_2)_4$ (**1**).¹⁷ This report describes studies of the scope and mechanism of this reaction, together with related chemistry of aziridines, CH_2CH_2NR . A variety of mechanistic data (the stereochemistry of de-epoxidation, the relative reactivity of different epoxides, labeling experiments, and other studies) argue against mechanisms involving oxametallacyclobutane or long-lived radical, carbocation,

(1) PRF Summer Faculty Fellow. Present address: North Seattle Community College, 9600 College Way N., Seattle, WA 98103.

(2) Presidential Young Investigator, 1988-1993. Alfred P. Sloan Research Fellow, 1989-1991.

(3) (a) Sheldon, R. A.; Kochi, J. K. *Metal-Catalyzed Oxidation of Organic Compounds*; Academic Press: New York, 1981; especially Chapter 6. (b) Jørgensen, K. A. *Chem. Rev.* **1989**, *89*, 431-458. (c) Wong, H. N. C.; Fok, C. C. M.; Wong, T. *Heterocycles* **1987**, *26*, 1345-82. (d) Nugent, W. A.; Mayer, J. M. *Metal-Ligand Multiple Bonds*; Wiley-Interscience: New York, 1988; pp 248-51. The literature on epoxidation is extensive; only selected references are given below.

(4) (a) Groves, J. T.; Nemo, T. E.; Myers, R. S. *J. Am. Chem. Soc.* **1979**, *101*, 1032-3. (b) Groves, J. T.; Quinn, R. *J. Am. Chem. Soc.* **1985**, *107*, 5790-2. (c) Groves, J. T.; Stern, M. K. *J. Am. Chem. Soc.* **1988**, *110*, 8628-38 and references therein. (d) Groves, J. T.; Myers, R. S. *J. Am. Chem. Soc.* **1983**, *105*, 5791-6. (e) Groves, J. T.; Watanabe, Y. *J. Am. Chem. Soc.* **1986**, *108*, 507-8.

(5) Lindsay-Smith, J. R.; Sleath, P. R. *J. Chem. Soc., Perkin Trans. 2* **1982**, 1009-15.

(6) (a) Traylor, T. G.; Xu, F. *J. Am. Chem. Soc.* **1988**, *110*, 1953-8. (b) Traylor, T. G.; Nakano, T.; Miksztal, A. R.; Dunlap, B. E. *J. Am. Chem. Soc.* **1987**, *109*, 3625-32. (c) Traylor, T. G.; Miksztal, A. R. *J. Am. Chem. Soc.* **1987**, *109*, 2770-4. (d) Traylor, T. G.; Miksztal, A. R. *J. Am. Chem. Soc.* **1989**, *111*, 7443-8.

(7) (a) Srinivasan, K.; Michaud, P.; Kochi, J. K. *J. Am. Chem. Soc.* **1986**, *108*, 2309-20. (b) Miyaura, N.; Kochi, J. K. *J. Am. Chem. Soc.* **1983**, *105*, 2368-78.

(8) (a) Collman, J. P.; Kodadek, T.; Raybuck, S. A.; Brauman, J. I.; Papazian, L. M. *J. Am. Chem. Soc.* **1985**, *107*, 4343-5. (b) Collman, J. P.; Brauman, J. I.; Meunier, B.; Hayashi, T.; Kodadek, T.; Raybuck, S. A. *J. Am. Chem. Soc.* **1985**, *107*, 2000-5. (c) Collman, J. P.; Hampton, P. D.; Brauman, J. I. *J. Am. Chem. Soc.* **1990**, *112*, 2986-2998.

(9) (a) Castellino, A. J.; Bruce, T. C. *J. Am. Chem. Soc.* **1988**, *110*, 158-62, 7512-9. (b) Garrison, J. M.; Bruce, T. C. *Ibid.* **1989**, *111*, 191-8. (c) Garrison, J. M.; Ostovic, D.; Bruce, T. C. *Ibid.* **1989**, *111*, 4960-6. (d) Ostovic, D.; Bruce, T. C. *Ibid.* **1989**, *111*, 6511-7.

(10) Meunier, B.; Guilmet, E.; De Carvalho, M.-E.; Poilblanc, R. *J. Am. Chem. Soc.* **1984**, *106*, 6668-76.

(11) Dobson, J. C.; Seok, W. K.; Meyer, T. J. *Inorg. Chem.* **1986**, *25*, 1513-4.

(12) Kinneary, J. F.; Albert, J. S.; Burrows, C. J. *J. Am. Chem. Soc.* **1988**, *110*, 6124-9. Yoon, H.; Burrows, C. J. *Ibid.* **1988**, *110*, 4087-9.

(13) Theoretical studies: (a) Rappè, A. K.; Goddard, W. A., III *J. Am. Chem. Soc.* **1982**, *104*, 448-56. (b) Jørgensen, K. A.; Hoffmann, R. *J. Am. Chem. Soc.* **1986**, *108*, 1867-76. (c) Schiøtt, B.; Jørgensen, K. A. *J. Chem. Soc., Dalton Trans.* **1989**, 2099-107. (d) Calhorda, M. J.; Hoffmann, R.; Friend, C. M. *J. Am. Chem. Soc.* **1990**, *112*, 50-61.

(14) Other examples of deoxygenation of epoxides to olefins by transition-metal complexes: (a) Sharpless, K. B.; Umbreit, M. A.; Nieh, M. T.; Flood, T. C. *J. Am. Chem. Soc.* **1972**, *94*, 6538-40. (b) Berry, M.; Davies, S. G.; Green, M. L. H. *Chem. Commun.* **1978**, 99-100. (c) Togashi, S.; Fulcher, J. G.; Cho, B. R.; Hasegawa, M.; Gladysz, J. A. *J. Org. Chem.* **1980**, *45*, 3044-53. (d) Kochi, J. K.; Singleton, D. M.; Andrews, L. *J. Tetrahedron* **1968**, *24*, 3503-15. (e) Moloy, K. G. *Inorg. Chem.* **1988**, *27*, 677-81. (f) Whinnery, L. L., Jr.; Bercaw, J. E. *Abstracts of Papers*, 196th ACS National Meeting, Los Angeles CA, Sept 1988, Inorganic Abstract No. 160. (g) McMurry, J. E.; Fleming, M. P. *J. Org. Chem.* **1975**, *40*, 2555. (h) Evans, W. J.; Grate, J. W.; Bloom, I.; Hunter, W. E.; Atwood, J. L. *J. Am. Chem. Soc.* **1985**, *107*, 405-9. (i) Schobert, R. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 855-6. (j) Deoxygenation by a Mo surface: Serafin, J. G.; Friend, C. M. *J. Am. Chem. Soc.* **1989**, *111*, 6019-26.

(15) Hucknall, D. J. *Selective Oxidation of Hydrocarbons*; Academic Press: New York, 1974. Cullis, C. F.; Hucknall, D. J. *Catalysis (Specialist Periodical Reports)* Roy. Soc. Chem. **1982**, *5*, 273. Parshall, G. W. *Homogeneous Catalysis*; Wiley-Interscience: New York, 1980; pp 115-7.

(16) *Cytochrome P-450: Structure, Mechanism, and Biochemistry*; P. R. Ortiz de Montellano, Ed.; Plenum Press: New York, 1986.

(17) (a) Su, F. M.; Bryan, J. C.; Jang, S.; Mayer, J. M. *Polyhedron* **1989**, *8*, 1261-77. (b) Bryan, J. C.; Geib, S. J.; Rheingold, A. L.; Mayer, J. M. *J. Am. Chem. Soc.* **1987**, *109*, 2826-8.

Table I. Stereochemistry of De-epoxidation by $WCl_2(CH_2CH_2)_2(PMePh_2)_2$ (**2**)

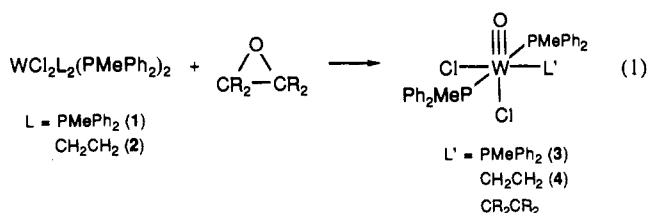
epoxide	% cis olefin ^a	% trans olefin ^a
<i>cis</i> -2-butene oxide	91	9
<i>trans</i> -2-butene oxide	12	88
<i>cis</i> - β -methylstyrene oxide	85	15
<i>trans</i> - β -methylstyrene oxide	4	96
<i>cis</i> -5-decene oxide	$\geq 91^b$	
<i>trans</i> -5-decene oxide		$\geq 99^b$

^aRelative yields of olefins, determined by NMR for the first two entries and by GC for the last. ^bData from Nugent.²¹

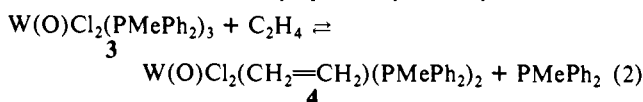
or carbanion intermediates. The data are most consistent with concerted oxygen or nitrene transfer to tungsten or with a mechanism involving a short-lived radical intermediate.

Results

$WCl_2(PMePh_2)_4$ (**1**) and $WCl_2(CH_2=CH_2)_2(PMePh_2)_2$ (**2**) each react with a variety of epoxides within a day at ambient temperatures to form tungsten(IV)-oxo complexes, $W(O)Cl_2(L')(PMePh_2)_2$ (eq 1).¹⁷ The nature of the sixth ligand in the

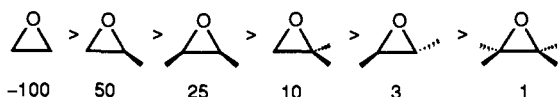


product, L', depends on the ligands present in solution and their concentrations; in general, equilibrium mixtures are obtained. The oxo-ethylene complex $W(O)Cl_2(CH_2=CH_2)(PMePh_2)_2$ (**4**) is the predominant product when ethylene is available, either from deoxygenation of ethylene oxide or in reactions of **2**. The equilibrium constant relating the tris(phosphine) and ethylene complexes (eq 2) is roughly 500 (by NMR). Reactions of **1** with disubstituted or more bulky epoxides yield only **3**.

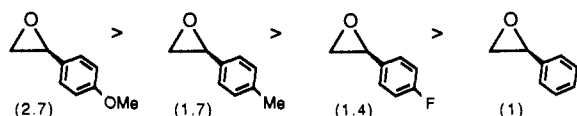


Complex **2** reacts with epoxides (and other substrates) at a rate that is not very sensitive to the nature or the concentration of the epoxide but is substantially slower in the presence of added ethylene. No reaction is observed between **2** and ethylene. The first step in reactions of **2** is therefore dissociation of ethylene. The reaction of **2** with epoxides under pseudo-first-order conditions (excess epoxide) occurs with an initial rate constant of roughly 10^{-2} s^{-1} , but it slows as ethylene is formed, presumably because ethylene competes with the epoxide for the unsaturated intermediate $WCl_2(CH_2CH_2)(PMePh_2)_2$. Complex **1** is in general more reactive than **2**, but its reactions are not limited by the rate of phosphine loss, which is fast.

The relative reactivities of a number of epoxides with **2** have been determined by competition experiments, with the conclusion that more substituted epoxides are deoxygenated less readily:



The reactivity of styrene oxide with **2** is enhanced by electron donating or potentially conjugating para substituents:

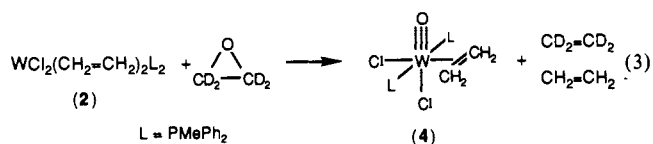


Styrene oxide reacts not only with **1** and **2** but also with the tungsten(IV)-oxo complex **3**. Complex **4** is inert to styrene oxide,

presumably because the ethylene ligand is less labile than the phosphine in **3**.

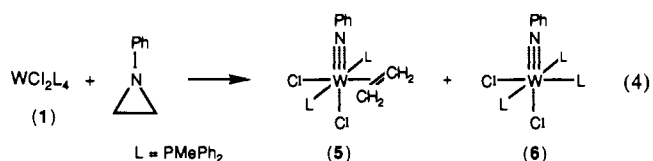
Deoxygenation by **2** proceeds principally, although not entirely, with retention of configuration, as summarized in Table I. For instance, *cis*-2-butene oxide yields roughly 91% *cis*- and 9% *trans*-2-butene. Neither the starting epoxide nor the product alkene is isomerized under the reaction conditions, as revealed by in situ NMR monitoring. Similarly, added 2-butene is not isomerized during the deoxygenation of 1,2-epoxybutane.

The reaction of **2** with ethylene-*d*₄ oxide (eq 3) yields uncoordinated $CD_2=CD_2$ in solution and the ethylene ligand in **4** is $CH_2=CH_2$, by ¹H and ²H NMR spectroscopy. Integration of



the NMR spectra places an upper limit of 10% on the amount of C_2D_4 bound to tungsten. The exchange of bound and free ethylene in **4** is slow on the time scale of this experiment. Thus the ethylene ligand in the tungsten product is one of the ethylenes present in **2**, not the ethylene formed from the epoxide.

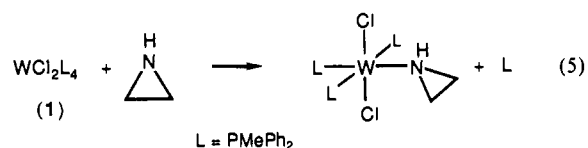
Aziridines ($RNCH_2CH_2$) and episulfides react similarly with tungsten(II) compounds to give imido and sulfido complexes.^{17a} For instance, **1** reacts with *N*-phenylaziridine to give the known^{17a,18} phenylimido complexes **5** and **6** (eq 4). In the initial



stages **6** is the dominant product but the final ratio of **5** to **6** is roughly 2:1. Early in the reaction, the ethylene formed may bind preferentially to the tungsten(II) starting material, but as this is consumed, the ethylene reacts with **6** to form **5**.^{17a}

Reaction 4 requires one month at ambient temperatures to go to completion, in contrast to the epoxide reactions that are complete within a day at 25 °C. The size of the aziridine substituent has a large effect on the rate of reaction: The larger *tert*-butyl derivative does not react appreciably with **1** after a month at 25 °C, while *N*-methylaziridine reacts with **1** or **2** over a day to give primarily the methylimido analogue of **5**, $W(NMe)Cl_2(CH_2CH_2)(PMePh_2)_2$, identified by NMR. From a competition experiment, *N*-methylaziridine is roughly as reactive with **2** as

isobutylene oxide. The parent aziridine, CH_2CH_2NH , reacts rapidly with **1** to give a bright red intermediate that decays within minutes to an apparent mixture of imido complexes (by NMR). The red species has a paramagnetic NMR spectrum, shifted but sharp, very similar to the amine adducts $WCl_2(NH_2R)(PMePh_2)_3$ formed on reaction of **1** with amines such as methyl amine,¹⁹ so the intermediate is most likely a simple adduct, **7** (eq 5).

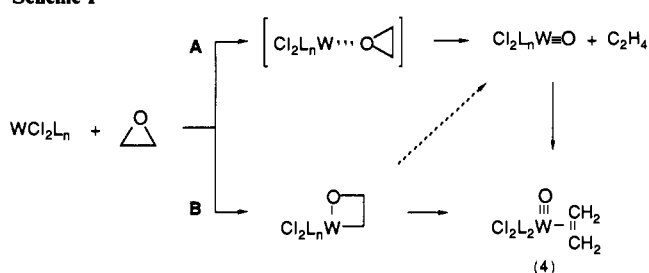


Discussion

A variety of mechanisms have been suggested for the epoxidation of olefins by metal-oxo complexes and for the reverse process, the deoxygenation of epoxides to form metal-oxo species.³⁻¹⁴ For the reactions described here, the observation of

(18) Nielson, A. J. *Inorg. Synth.* **1986**, *24*, 194-200. Clark, G. R.; Nielson, A. J.; Rickard, C. E. F.; Ware, D. C. *Chem. Commun.* **1989**, 343-5.
 (19) Over, D. E.; Mayer, J. M. Unpublished results.

Scheme I



predominant retention of configuration (Table I) rules out long-lived radical, carbocation, or carbanion intermediates.²⁰ In addition, Nugent has found that the deoxygenation of 1,6-heptadiene monoepoxide by **1** yields only 1,6-heptadiene, with no evidence for products resulting from radical cyclization.²¹ Predominant retention of configuration has been observed in de-epoxidation by tungsten, molybdenum, and tantalum complexes^{14a,e,f} and is usually, although not always, observed in epoxidation by metal-oxo compounds.^{3,22} Radical intermediates have been invoked to explain loss of stereochemistry in de-epoxidation reactions of Cp_2TiCl_2 ²³ and in epoxidations by oxo-manganese compounds.^{4c}

The two types of mechanisms frequently suggested to explain stereoretention are oxygen atom transfer and a pathway involving an oxametallacycle (Scheme I). Direct oxygen atom transfer (path A) is a common reaction of metal-oxo complexes^{24,25} and has been suggested as the mechanism of deoxygenation of epoxides by a tantalum complex^{14f} and as a mechanism of epoxidation by iron- and ruthenium-oxo complexes.^{9c,11} Reduction of epoxides and episulfides by a molybdenum(110) surface apparently occurs by a similar pathway.^{14j,26} In 1977 Sharpless et al. suggested²⁷ a mechanism for olefin oxidations involving olefin coordination to the metal center and rearrangement to an oxametallacyclobutane. Epoxides are formed by reductive elimination. In the reverse direction (path B in Scheme I), deoxygenation would proceed by oxidative addition of an epoxide C-O bond followed by rearrangement to an oxo-olefin complex.

The reaction of **2** with ethylene-*d*₄ oxide described above (eq 3) is consistent with mechanism A, direct oxygen atom transfer from epoxide to tungsten, since $\text{CD}_2=\text{CD}_2$ is released into the solution and is not observed coordinated to tungsten. This result is harder to reconcile with path B, in particular the rearrangement of an oxametallacycle to an oxo-olefin complex: one would have to assume that the oxo-bis(ethylene) complex formed selectively

(20) Carbocation intermediates have been proposed in a number of epoxidation reactions.^{4d,6,9} Radical intermediates have been suggested in epoxidations by oxo-manganese (and perhaps nickel¹²) compounds to account for the loss of stereochemistry.^{3,4c,7a,1b} The reactions of oxo-iron species have been suggested to proceed through initial electron transfer, forming an olefin radical cation which subsequently binds to the oxo group.^{6,9} A radical cation is unlikely in the reducing tungsten systems described here. Initial outersphere electron transfer from tungsten to the epoxide, forming an epoxide radical anion, is also unlikely. **1** and **2** are not good outersphere reducing agents, for instance **1** does not react with 3-pentanone (which should be more easily reduced than an epoxide).²⁹ Outersphere electron transfer is also inconsistent with rate-limiting loss of ethylene from **2**. In addition, the epoxide radical anion should ring open and therefore lose stereochemistry; in general, epoxide deoxygenations by strong one-electron reductants (e.g. Li, SmI_2) are not stereospecific.^{3c}

(21) Nugent, W. A., Central Research and Development Department, E. I. DuPont de Nemours and Co., personal communication, 1988.

(22) Epoxidation with predominant retention of configuration is common for iron-oxo,^{4a,9} ruthenium-oxo,^{4b,11} and chromium-oxo species^{7b,9c} while both retention and loss of stereochemistry are reported for manganese-oxo species.^{4c,7a,8-10}

(23) Nugent, W. A.; RajanBabu, T. V. *J. Am. Chem. Soc.* **1988**, *110*, 8561-2. RajanBabu, T. V.; Nugent, W. A. *Ibid.* **1989**, *111*, 4525-7. RajanBabu, T. V.; Nugent, W. A.; Beattie, M. S. *Ibid.* **1990**, *112*, 6408-9.

(24) Hohm, R. H. *Chem. Rev.* **1987**, *87*, 1401-9.

(25) Reference 1d, p 241ff.

(26) Roberts, J. T.; Friend, C. M. *J. Am. Chem. Soc.* **1987**, *109*, 7899-900. Friend, C. M.; Roberts, J. T. *Acc. Chem. Res.* **1988**, *21*, 394-400. Roberts, J. T.; Friend, C. M. *Surf. Sci.* **1988**, *202*, 405. See also ref 13d.

(27) Sharpless, K. B.; Teranishi, A. Y.; Bäckvall, J. E. *J. Am. Chem. Soc.* **1977**, *99*, 3120-8. Hentges, S. G.; Sharpless, K. B. *Ibid.* **1980**, *102*, 4263-5.

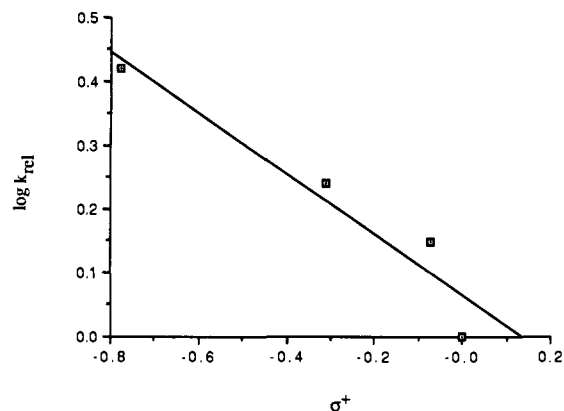
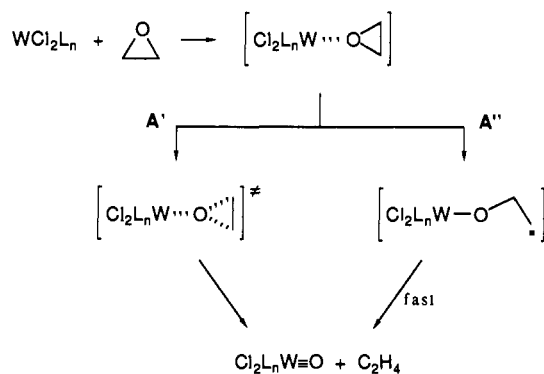


Figure 1. Hammett plot of the relative reactivity of para-substituted styrene oxides versus σ^+ constants. From left to right, the substituents are methoxy, methyl, fluoro, and hydrogen.

Scheme II



dissociates the olefin that was originally present in the epoxide. The labeling study is also consistent with decomposition of the oxametallacycle by direct loss of ethylene into solution (the dotted line in Scheme I), as recently suggested for a tantalum oxametallacycle,²⁸ but this seems a little less likely as loss of olefin from metallacyclobutanes is believed to proceed via carbene-olefin complexes.²⁹

Another difference between mechanisms A and B is the initial site of attack of the tungsten(II) center: in path A attack occurs at the oxygen (or at nitrogen for aziridines) and in path B likely at a C-O (or C-N) bond. The observation of the aziridine adduct **7** suggests path A. Initial nitrogen coordination is also supported by the observation that steric bulk at nitrogen strongly inhibits the reaction, since sterics also strongly inhibit amine coordination to tungsten(II).¹⁹ Attack at a C-N bond to form an azametallacyclobutane should be less sensitive to the aziridine substituent because the substituent has little effect on the reactions of **1** with imines (e.g. *N*-TolylN=CMe₂) and isocyanates, which appear to involve tungsten binding to the C-N π bond.³⁰ For instance, *tert*-butyl and *p*-tolyl isocyanates react at roughly the same rate, comparable to the rate of cleavage of unhindered C=O and C=S bonds in CO₂, OCS, and RNCS.^{17,30}

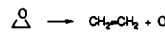
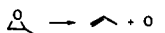



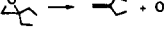
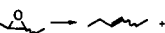
The relative epoxide reactivities also appear to support mechanism A. The reactivities of ethylene, isobutylene, and tetramethylethylene oxides fall in a geometric progression (100:10:1), suggesting that the transition state for deoxygenation has a similar environment for the two carbons. This is also suggested by the placement of isobutylene oxide midway in between *cis*- and *trans*-2-butene oxide. In the formation of a metallacycle, however, the tetrasubstituted epoxide should be much slower than ethylene and isobutylene oxides because two methyl groups would have to be in a sterically crowded site next to the metal center. This

(28) Whinnery, L. L., Jr.; Bercaw, J. E. Personal communication, 1988 and ref 14f.

(29) Anslyn, E. V.; Grubbs, R. H. *J. Am. Chem. Soc.* **1987**, *109*, 4880-90.

(30) Bryan, J. C.; Mayer, J. M. *J. Am. Chem. Soc.* **1990**, *112*, 2298-308.

Table II. Heats of De-epoxidation (kcal/mol)^a

reaction	ΔH°	
	gas ^b	liquid ^c
	84.7	
	86.7	89.6
	92.1	94.8
	89.4	92.4
		100 ^d
		99 ^{d,e}
		105 ^d

^a Values calculated from heats of formation for the epoxide, the alkene, and an oxygen atom, from ref 35. ^b Calculated with gas-phase heats of formation. ^c Calculated with liquid-phase heats of formation for the epoxide and the alkene. For propene and 1-butene, ΔH_f° is given at the saturation pressure.^{35a} ^d Epoxide heat of formation taken from Stull et al.,^{35c} who could not verify the accuracy of the values. ^e The stereochemistry of the epoxide was not reported; the difference in ΔH_f° between the cis and trans olefins is only 0.4 kcal/mol.^{35c}

pattern of reactivity also argues against carbocation and radical intermediates, as isobutylene oxide should form a carbocation or radical of roughly equal stability to that from tetramethylethylene oxide.

The relative reactivities of substituted styrenes correlate fairly well with the Hammett σ^+ parameters, yielding a ρ^+ value of -0.5 (Figure 1). The correlation is worse with σ parameters ($R^2 = 0.92$; $R^2 = 0.72$). This is clear from the reactivity order, p -OMe $>$ p -Me $>$ p -F $>$ H, because the σ parameters place fluoro on the other side of H.³¹ Correlation with σ^+ parameters indicates that there is conjugation between the phenyl ring and the α carbon of the epoxide, and the negative ρ indicates that the phenyl ring acts as an electron donor. The calculated ρ^+ value of -0.5 is small, however, so there is little charge buildup in the transition state. For comparison, the S_N1 solvolysis of 2-aryl-2-chloropropanes in aqueous acetone gives a ρ^+ of -4.5 (the p -methoxy derivative reacts $>10^3$ times faster than the phenyl).³¹ Addition of CCl_2 to styrenes, which has a ρ^+ value of -0.62 , is believed to be concerted with a slightly polar transition state.³² Epoxidation of substituted stilbenes by perbenzoic acid, also thought to be concerted, gives $\rho^+ = -1.2$.³³ ρ^+ values for epoxidation by metal oxo-porphyrin species are typically -0.4 to -0.9 ,^{8c} although values as high as -1.9 have been reported.^{4e,9c}

The conclusion that there are no long-lived intermediates is consistent with either concerted oxygen atom transfer or the presence of a short-lived species (paths A' and A'' in Scheme II). A short-lived intermediate, if involved, is more likely a radical than a carbocation or carbanion species based on the Hammett analysis. Reduction of epoxides by Cr^{II} and Ti^{III} has been suggested to proceed through a ring-opened radical, $\text{M}-\text{O}-\text{CR}_2\text{CR}_2^{\cdot}$ ($\text{M} = \text{Cr}^{\text{II}}, \text{Ti}^{\text{III}}$).^{14d,23} In the tungsten case, given the stability of the $\text{W}^{\text{IV}}=\text{O}$ bond, this radical might be expected to very rapidly lose alkene (path A''). The radical mechanism appears to be favored over a concerted pathway by the partial loss of stereochemistry on deoxygenation, although this could occur through a second mechanistic pathway. On the other hand, the effects of increasing substitution suggest a symmetrical transition state, as in a concerted process. One recent theoretical study of this reaction supports a concerted mechanism,^{13c} but another indicates that the very similar loss of ethylene from coordinated ethylene sulfide is forbidden.^{13d}

Increasing substitution of the epoxide slows the rate of deoxygenation. In contrast, epoxidation of olefins is known to be

favored by increasing olefinic substitution.³⁴ This is a result of the thermodynamics of the reaction: more substituted olefins are more electron rich and are therefore easier to oxidize, and the epoxides are harder to reduce. This trend is shown quantitatively in the enthalpies of deoxygenation of epoxides (Table II), calculated from the heats of formation of the epoxide, the olefin, and an oxygen atom.³⁵ (Although the trend is clear, it should be noted that the accuracy of the last three values in Table II could not be confirmed by the authors of ref 34c.) Given the significant change in driving force from one epoxide to another, it is clear that thermodynamic considerations must be explicitly included in our understanding of these reactions. In fact it is surprising that ethylene oxide and tetramethylethylene oxide are only a factor of a hundred different in reactivity, corresponding to a difference of roughly 2 kcal/mol in activation energy. Peracetic acid epoxidation of $\text{CMe}_2=\text{CMe}_2$ is 58 000 times faster than oxidation of $\text{CH}_2=\text{CH}_2$.^{34a} The small range of reactivity in this system indicates an early transition state. An early transition state is expected for these reactions, if the mechanism is concerted, because they are highly exothermic. The reaction with ethylene oxide, for instance, is estimated to be >30 kcal/mol downhill, on the basis of 1 reacting similarly with CO_2 which is 37 kcal/mol harder to deoxygenate than $\text{CH}_2\text{CH}_2\text{O}$.³⁶

cis-2-Butene oxide is deoxygenated more rapidly than the trans isomer in reactions with 2. Similarly, cis olefins are usually epoxidized faster than trans isomers by metal-oxo species.^{3,4a,5,6a,7a,8,10} If there is a common mechanism, this suggests that the transition state in both directions is more stable for cis isomers, probably for steric reasons.^{4d}

Conclusions

The reactions of epoxides and aziridines with 1 and 2 appear to involve initial coordination of the substrate oxygen or nitrogen atom to the tungsten(II) center, as revealed, for instance, by the observation of an aziridine adduct. Long-lived radical, carbocation, or carbanion species are not involved because there is predominant retention of stereochemistry. Labeling studies and substituent effects suggest that the reactions do not proceed through oxo- or azametallacyclobutane intermediates. The reactions occur without substantial buildup of charge in the transition state, based on a Hammett analysis of the relative rates of deoxygenation of substituted styrene oxides.

The mechanistic data are most consistent with either (i) concerted oxygen atom or nitrene group transfer to tungsten or (ii) the formation of a short-lived radical species, $\text{W}^{\text{III}}-\text{O}-\text{CR}_2\text{CR}_2^{\cdot}$, which rapidly loses alkene (Scheme II). The concerted mechanism is suggested by the relative rates of differently substituted epoxides, for instance that the reactivity of isobutylene oxide is midway in between ethylene oxide and $\text{CMe}_2\text{CMe}_2\text{O}$. The relatively small differences in reactivity between the epoxides suggests an early transition state, also consistent with a concerted process (and consistent with the high exothermicity of the reactions). On the other hand, the small loss of stereochemistry on deoxygenation ($\leq 15\%$) indicates the presence of a short-lived ring-opened intermediate or a second pathway. The two mechanisms may not be contradictory; an early transition state might appear to be concerted although ring-opening is asynchronous and proceeds through a short-lived radical intermediate. The mechanistic conclusions indicate that the reverse reactions, epoxidation and

(34) (a) Khalil, M. M.; Pritzkow, W. *J. Prakt. Chem.* **1973**, *315*, 58–64. (b) The effect of substitution on the rate of epoxidation seems to be large for iron-oxo porphyrins^{5,6a,8c} but small for manganese analogues.^{7a,8b}

(35) (a) ΔH_f° values for alkanes, alkenes, ethylene oxide, propylene oxide, and 1,2-butene epoxide from TRC Thermodynamic Tables, Texas A&M University, College Station TX. Two values are given for the heat of formation of 1-butene oxide in these tables; the one on page p 6150 is used here (not page 2-6150) following the advice of TRC. (b) *trans*-2-Butene epoxide: Douslin, D. R.; Good, W. D.; Finke, H. L.; Messerly, J. F.; Osborn, A. *U.S.N.T.I.S. AD Rep.*, No. 785481 (*Chem. Abstr.* CA82(21): 139070j). (c) Other epoxides: Stull, D. R.; Westrum, E. F., Jr.; Sinke, G. C. *The Chemical Thermodynamics of Organic Compounds*; Wiley: New York, 1969.

(36) The oxo-ethylene and oxo-carbonyl products of these reactions are in roughly thermoneutral equilibrium in the presence of CO and ethylene.

(31) March, J. *Advanced Organic Chemistry*; Wiley-Interscience: New York, 1985. Hammett, L. P. *Physical Organic Chemistry*, 2nd ed., McGraw Hill: New York, 1970; p 360ff. Well, P. R. *Chem. Rev.* **1963**, *63*, 171–219.

(32) Seyferth, D.; Mui, J. Y.-P.; Damrauer, R. *J. Am. Chem. Soc.* **1968**, *90*, 6182–6.

(33) Ogata, Y.; Tabushi, I. *J. Am. Chem. Soc.* **1961**, *83*, 3440–4.

its nitrogen analogue,³⁷ can occur by initial attack of an olefin directly at an oxo or imido ligand.

Experimental Section

$WCl_2(PMePh_2)_4$ (**1**) and $WCl_2(CH_2=CH_2)_2(PMePh_2)_2$ (**2**) were prepared following published procedures.³⁸ Epoxides were obtained from the following sources: ethylene oxide, Matheson; propylene oxide, 1-butene oxide, and (1*R*,2*R*)-(+)-1-phenylpropylene oxide, Aldrich; *cis*-2-butene oxide and isobutylene oxide, Farchan; *trans*-2-butene oxide, a generous gift from Professor Paul Hopkins, University of Washington. Epoxides of tetramethylethylene, *cis*- β -methylstyrene, *p*-methylstyrene, and *p*-fluorostyrene were prepared from the olefin and *m*-CPBA.³⁹ *p*-Methoxystyrene oxide was prepared from *p*-anisaldehyde and Me_3Si .⁴⁰ Ethylene- d_4 oxide was prepared by adding neat 2-bromoethanol- d_4 (Cambridge Isotope) to NaOH(s).⁴¹

N-p-Tolylaziridine was prepared as previously described.⁴² *N-tert*-butylaziridine was prepared following the preparation of the *N-n*-butyl derivative and was used as an ether solution.⁴³ *N*-methylaziridine was prepared from $MeNHCH_2CH_2OSO_3H$, formed from *N*-methylaminoethanol (Aldrich) and freshly distilled chlorosulfonic acid (Aldrich).⁴³ $MeNHCH_2CH_2SO_3H$ (15.4 g) was dissolved in 100 mL of 14% aqueous NaOH at 0 °C. This solution was slowly added to 5 mL of 14% NaOH refluxing in a distillation apparatus. The aziridine immediately distilled into a receiving flask containing 60 g of NaOH pellets and cooled to -78 °C. *N*-Methylaziridine was vacuum transferred out of the distillate onto fresh NaOH and stored at -12 °C; the yield was 49%.

Reactions were performed in sealed NMR tubes and the products identified by ¹H and ³¹P NMR spectra and comparison with authentic samples.¹⁷ In a typical procedure, an NMR tube sealed to a ground glass joint was charged with 15 mg (0.021 mmol) of **2** in the glovebox and

capped with a Teflon valve. The assembly was removed to a vacuum line, where the remaining materials were added as vapors by vacuum transfer; the solvent (0.4 mL of C_6D_6 , transferred from CaH_2), *cis*-2,3-epoxybutane (55 Torr in a 7.5 mL volume), and *trans*-2,3-epoxybutane (15 Torr in 25.7 mL). The tube was cooled to 78 K and sealed with a torch. A number of NMR spectra were taken over a period of hours or days with Varian VXR-300 and Bruker WM-500 spectrometers; a 15- or 30-s delay was used to obtain accurate integrals.

The reaction of **2** with 1,2-epoxybutane was shown to be inhibited by added ethylene: 0.40 mL of a solution of **2** (45 mg in 1.20 mL of C_6D_6) was added to each of two NMR tubes sealed to ground glass joints. 1,2-Epoxybutane (22 Torr in 25.7 mL volume) was transferred to both tubes at 78 K, and ethylene (22 Torr in 25.7 mL) was added to one of the tubes, which were then sealed with a torch. Monitoring by NMR showed that the reaction without ethylene was more rapid: for instance, after 30 and 77 min, the reaction had proceeded to 26% and 89% conversion without ethylene, 18% and 57% conversion in the presence of 0.5 equiv of ethylene in solution.

Reactions of *N*-methylaziridine with **1** and **2** give a number of products, especially at longer reaction times. ¹H and ³¹P NMR spectra of the reaction are consistent with the initial product being $W(NMe)Cl_2(CH_2=CH_2)(PMePh_2)_2$; it has not been isolated in pure form. ¹H NMR (C_6D_6) 2.34 (t, $J_{PH} = 4$ Hz, 6 H, PCH_3), 1.94 (t, $J_{PH} = 4$ Hz, 3 H, NCH_3), 2.05, 1.76 (each: m, 2 H, $CHH'=CHH'$; tentative assignments). ³¹P{¹H} NMR (C_6D_6) 4.0 ($^1J_{WP} = 236$ Hz).

The initial red C_6D_6 solution formed of **1** and aziridine has the following NMR spectrum (at 5 °C): 10.7 (8 H, *m*-Ph), 10.2 (2 H + 4 H, *p*-Ph (two overlapping)), 9.8 (4 H, *o*-Ph), 9.0 (8 H, *o*-Ph), 7.5 (4 H, *m*-Ph), 8.0, 6.8 (2 H each, $CHH'CHH'NH$), 4.3 (3 H, PCH_3), -1.5 (6 H, PCH_3). This spectrum is quite similar to that of, for instance, the methylamine adduct (C_6D_6 , 5 °C):¹⁹ 11.8 (8 H, *m*-Ph), 10.9, 10.4 (2 H + 4 H, *p*-Ph), 10.0 (4 H, *o*-Ph), 8.9 (8 H, *o*-Ph), 6.3 (3 H, CH_3NH_2), 3.2 (3 H, PCH_3), -3.7 (6 H, PCH_3). The aziridine adduct is not stable enough at ambient temperatures to record good NMR spectra; the spectra of both adducts broaden on cooling. The ¹H NMR spectrum of the CH_3NH_2 adduct at 25 °C is sharper than that at 5 °C and shows some spin-spin coupling, which supports the indicated assignments.¹⁹

Acknowledgment. We thank Dr. Jeff Bryan for initial studies of this reaction and Dr. Bill Nugent for sharing his results. This work was supported by the National Science Foundation, the Chevron Research Co., and the donors of the Petroleum Research Fund, administered by the American Chemical Society.

(37) Formation of an aziridine from an imido complex plus an olefin: Groves, J. T.; Takahashi, T. *J. Am. Chem. Soc.* **1983**, *105*, 2073-4. Mansuy, D.; Mahy, J.-P.; Dureault, A.; Bedi, G.; Battioni, P. *Chem. Commun.* **1984**, 1161-3.

(38) Sharp, P. R. *Organometallics* **1984**, *3*, 1217-23. Sharp, P. R.; Bryan, J. C.; Mayer, J. M. *Inorg. Synth.* In press.

(39) Hibbert, H.; Bent, P. *Organic Syntheses*; Wiley: New York, 1941; Collect. Vol. 1, p 494.

(40) Borredon, E.; Delmas, M.; Gaset, A. *Tetrahedron Lett.* **1982**, *23*, 5283-6.

(41) Cox, J. D.; Wame, R. J. *J. Chem. Soc.* **1951**, 1893.

(42) Appel, R.; Kleinstück, R. *Chem. Ber.* **1974**, *107*, 5-12.

(43) Elderfield, R. C.; Hageman, H. A. *J. Org. Chem.* **1949**, *14*, 605.